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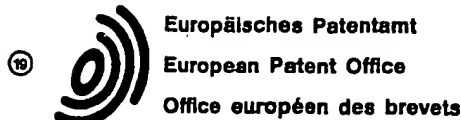
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0 277 842
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EUROPEAN PATENT APPLICATION

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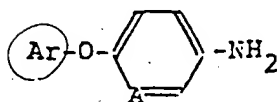
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Aromatic amine derivatives.

Aromatic amine derivatives of the formula



wherein Ar is an aromatic group comprising a benzene ring to which is fused an oxygen-containing heterocyclic group and A is a nitrogen atom



wherein X is hydrogen, chlorine, nitro or trifluoromethyl, are useful intermediate compounds for herbicides.

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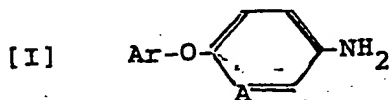
Aromatic Amine Derivatives

5 This invention relates to novel aromatic amine derivatives.

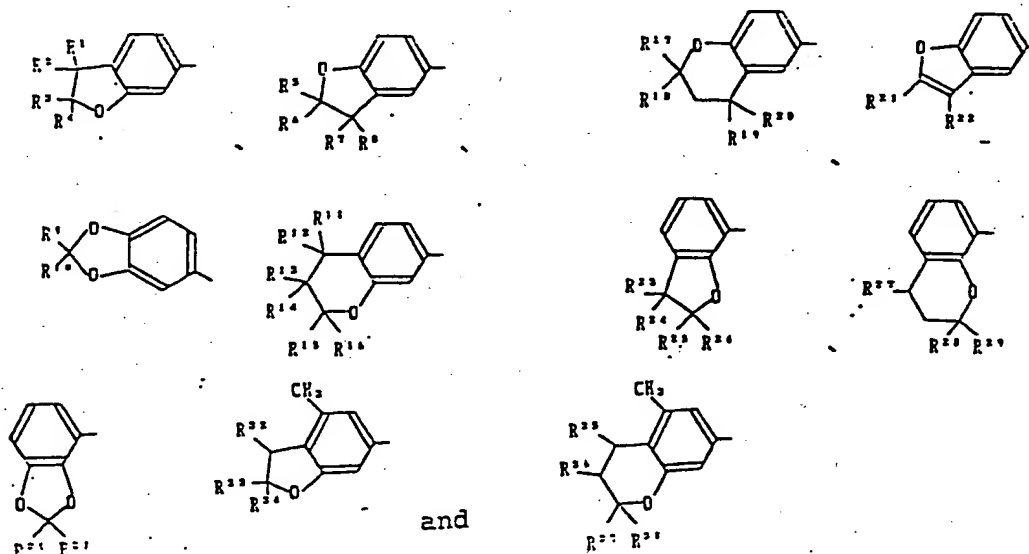
10 Making a research to produce a herbicide which is applicable in a small amount to kill weeds without phytotoxicity to growing crops, we have discovered novel aromatic amine derivatives which are useful as intermediates for herbicides meeting the above requirements.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a novel aromatic amine derivative of the general formula (I):



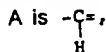
wherein Ar is a radical selected from the group consisting of



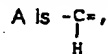
wherein R¹ to R¹⁵ and R¹⁷ to R³⁸ may be the same or different and are independently selected from the group consisting of hydrogen, lower alkyl radicals, and lower alkoxy radicals, R¹⁶ is selected from the group consisting of hydrogen, lower alkyl radicals, lower alkoxy radicals and hydroxyl, with the proviso that R² and R³, R⁶ and R⁷, R⁹ and R¹⁰, R¹¹ and R¹⁵, or R¹⁵ and R¹⁶ may, taken together, represent an alkylene chain, which may be substituted with a lower alkyl radical, to form a 5- or 6-membered ring with the carbon atoms to which they are attached, R¹¹ and R¹² may, taken together, represent an ethylene dioxy radical, or R¹⁴ and R¹⁵ may, taken together, represent a dichloromethylene radical; and

A is a nitrogen atom or $\begin{array}{c} -C= \\ | \\ Y \end{array}$

wherein X is selected from the group consisting of a hydrogen atom, a chlorine atom, a nitro radical, and a trifluoromethyl radical, when both R⁵ and R⁶ are methyl radicals and



at least one of R^7 and R^8 does not represent hydrogen atom, when both R^{25} and R^{26} are methyl radicals and



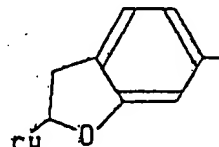
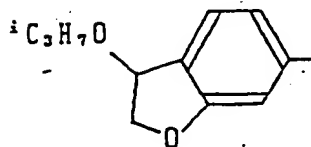
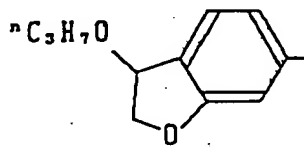
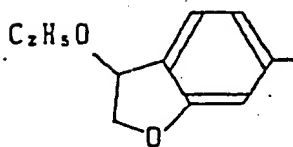
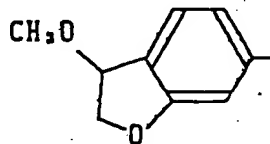
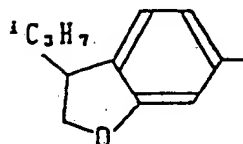
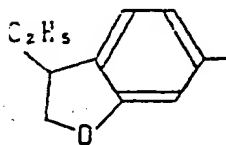
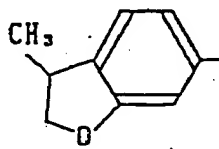
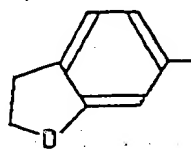
at least one of R^{23} and R^{24} does not represent hydrogen atom.

DETAILED DESCRIPTION OF THE INVENTION

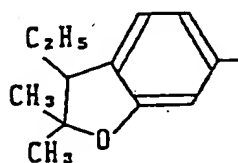
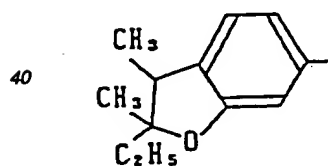
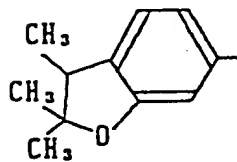
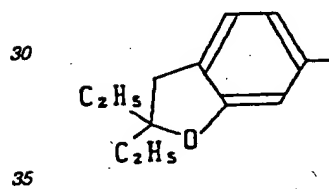
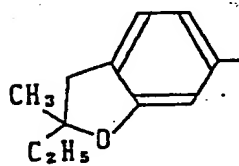
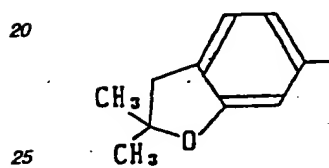
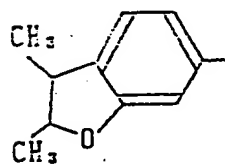
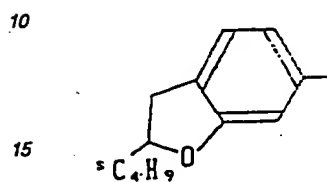
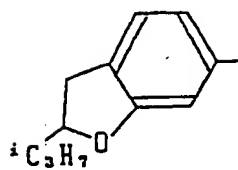
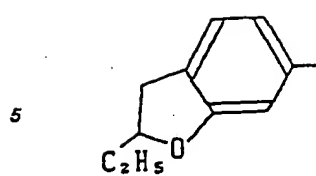
The aromatic amine derivatives of the present invention have the general formula [I] as defined above.

Examples of the lower alkyl radicals represented by R^1 through R^{38} include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, etc. Examples of the lower alkoxy radicals represented by R^1 through R^{38} include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, etc.

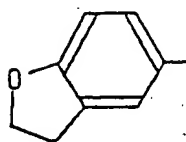
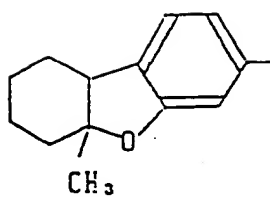
Examples of the radicals represented by Ar are shown below.



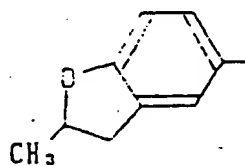
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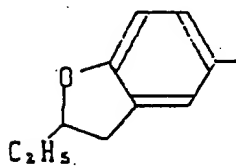
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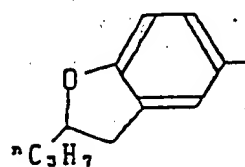
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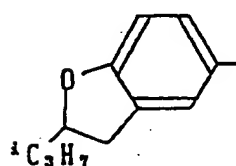
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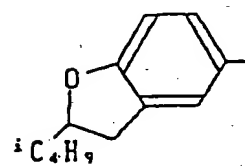
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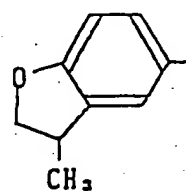
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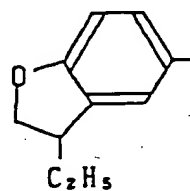
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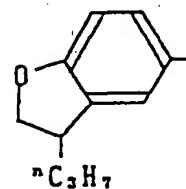
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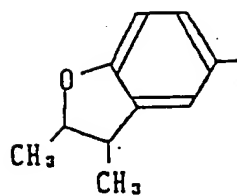
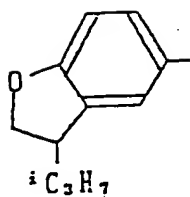
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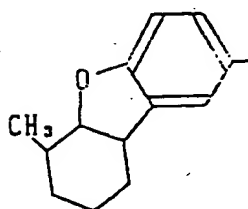
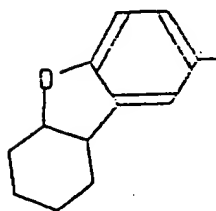
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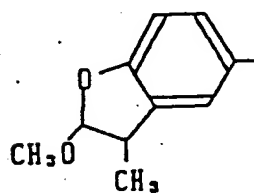
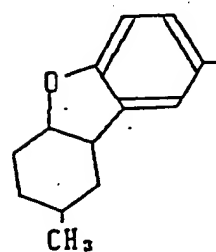


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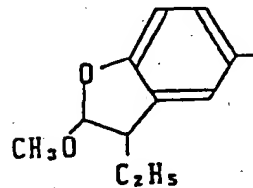
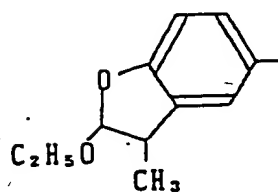
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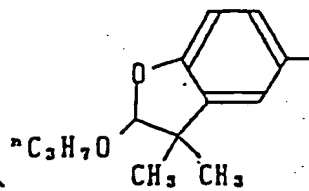
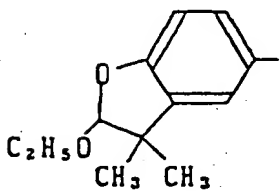
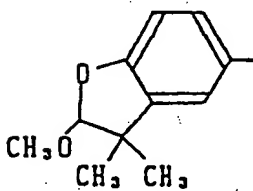
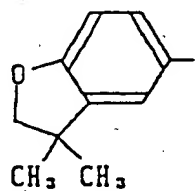
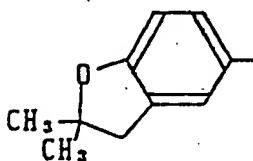
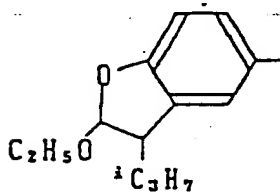
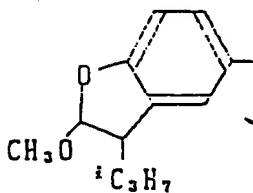
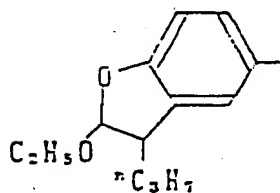
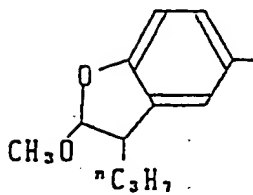
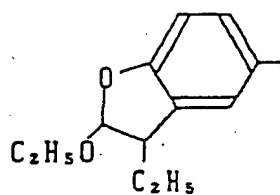
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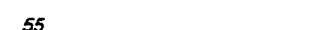
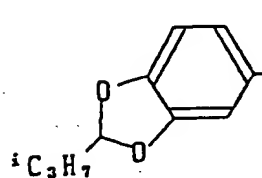
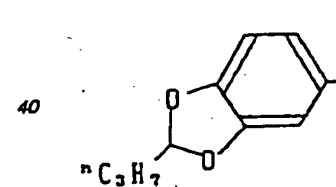
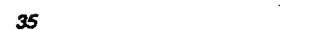
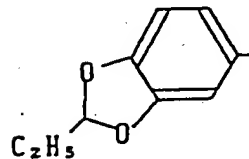
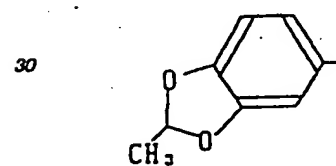
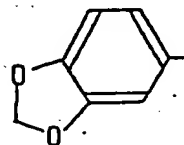
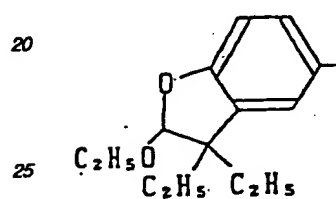
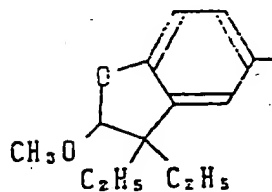
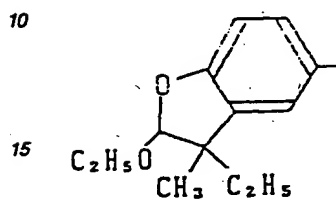
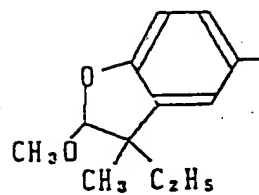
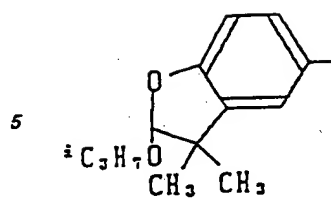
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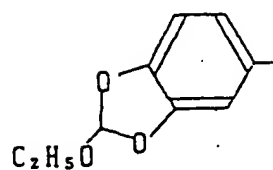
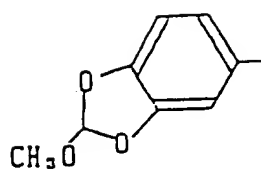
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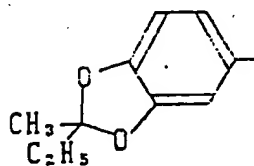
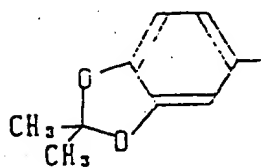
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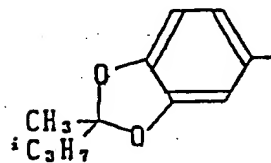
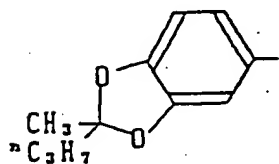


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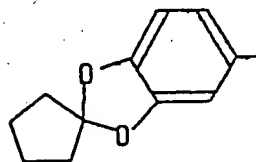
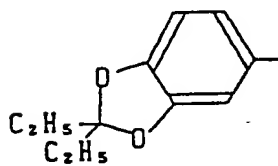
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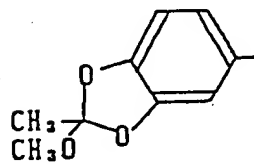
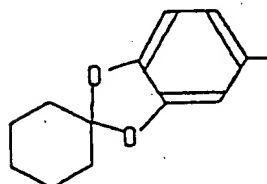
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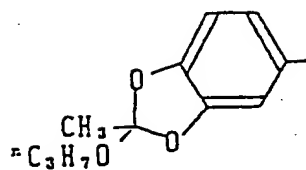
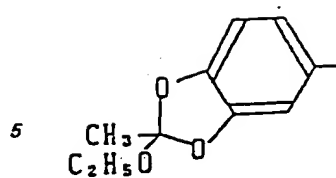
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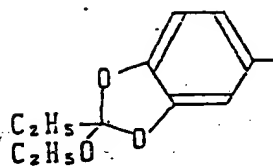
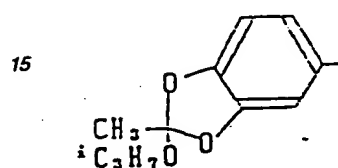
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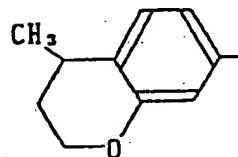
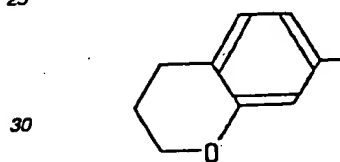


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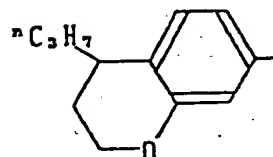
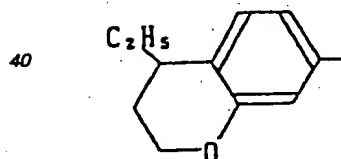


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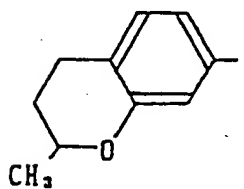
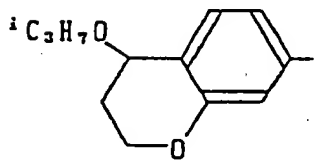
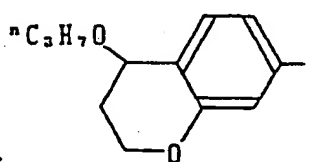
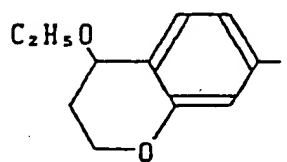
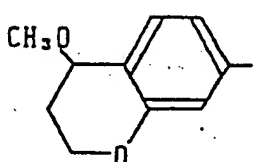
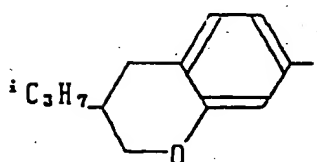
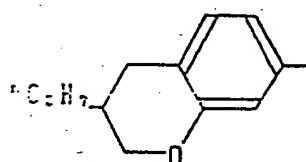
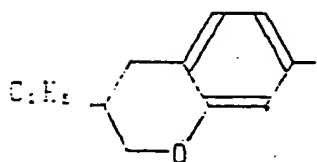
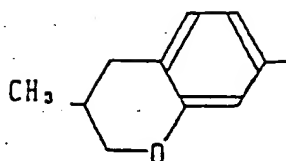
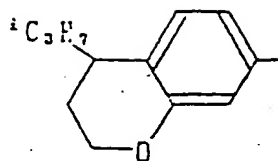
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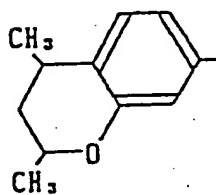
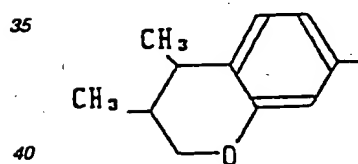
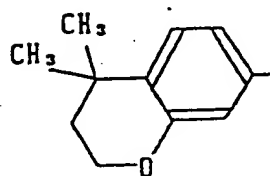
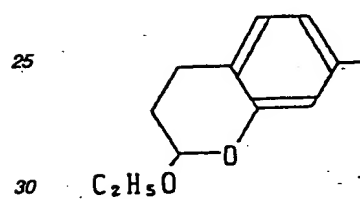
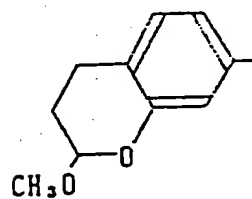
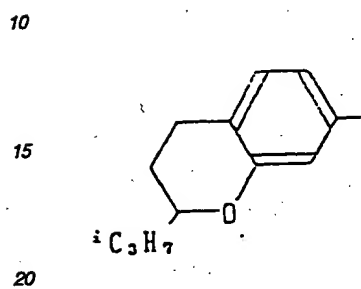
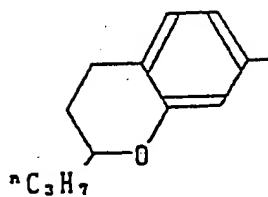
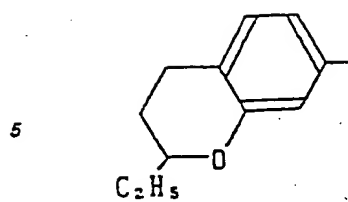
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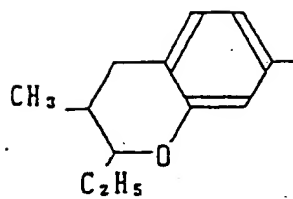
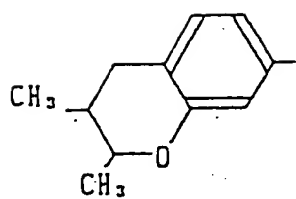
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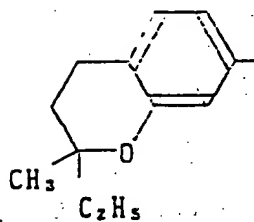
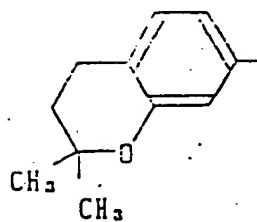
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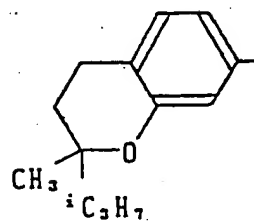
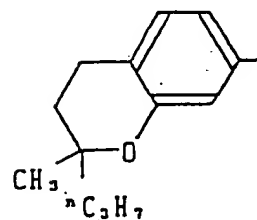
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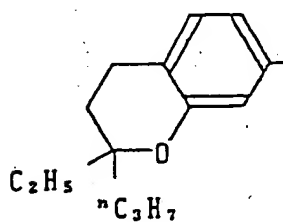
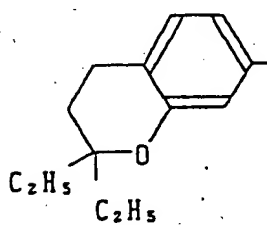
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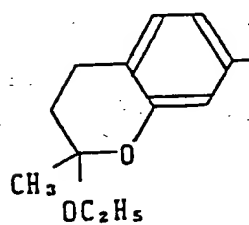
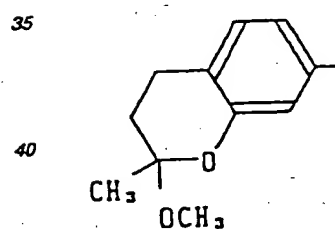
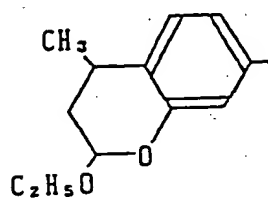
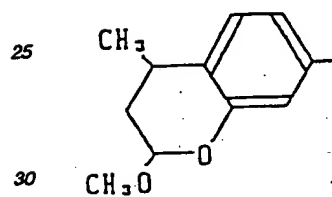
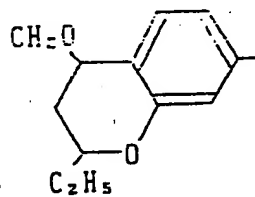
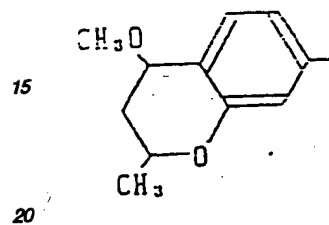
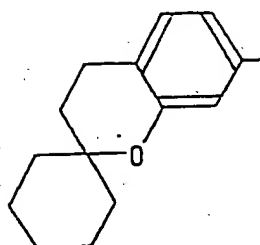
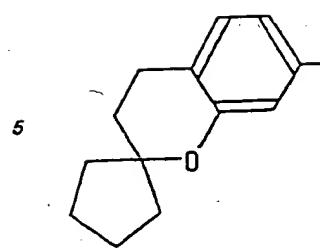
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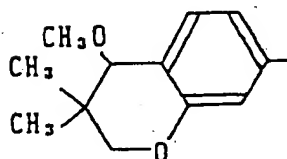
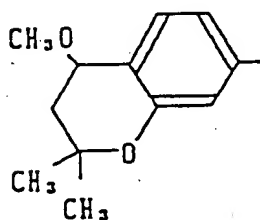
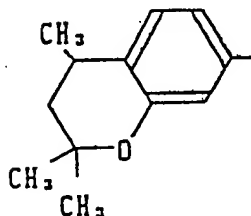
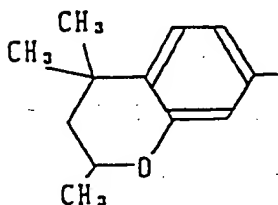
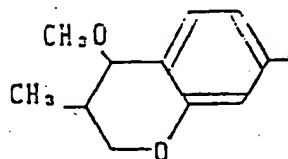
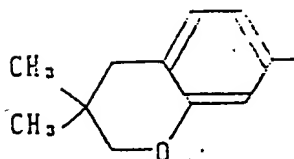
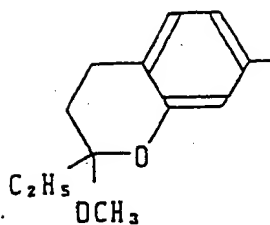
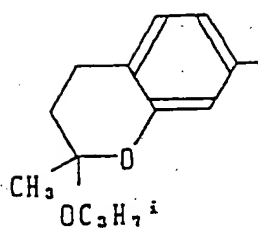
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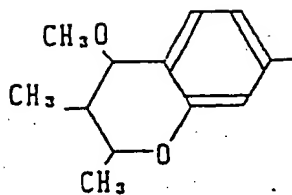
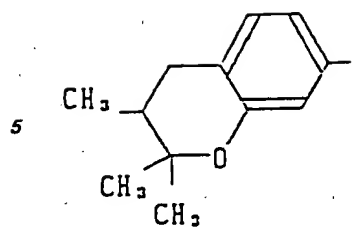
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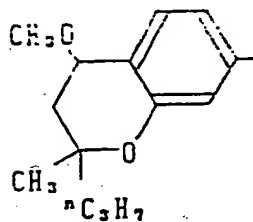
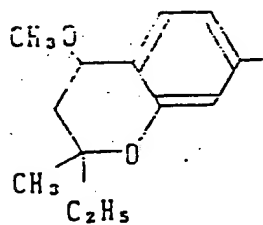
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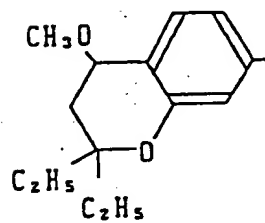
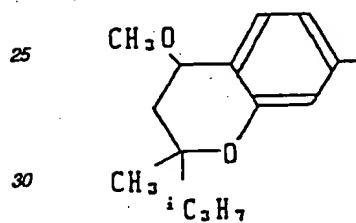
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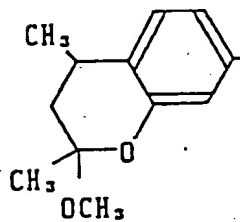
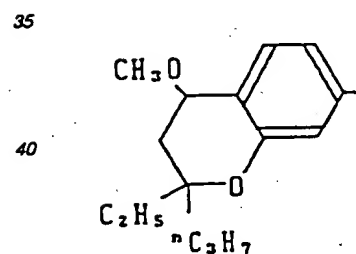
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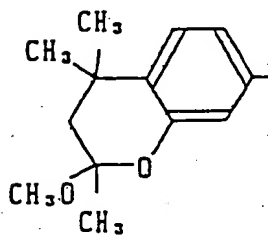
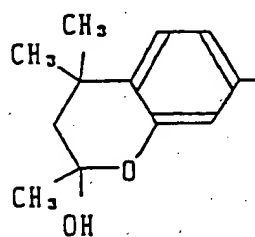
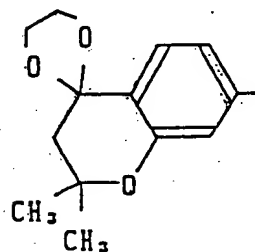
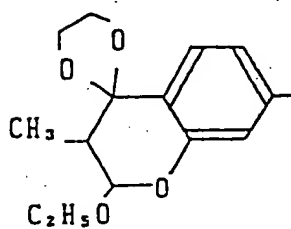
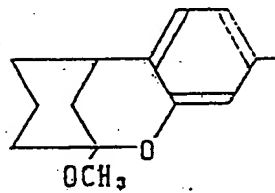
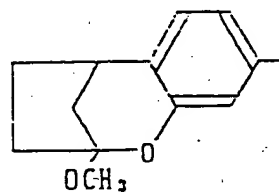
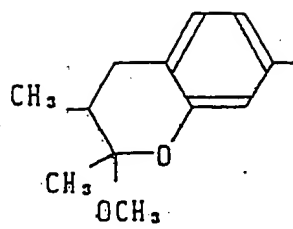
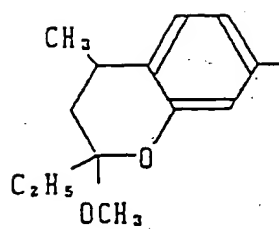
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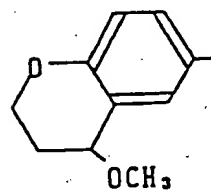
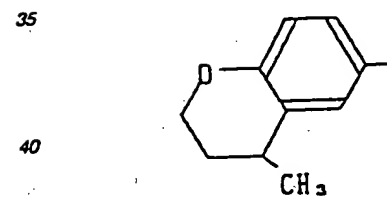
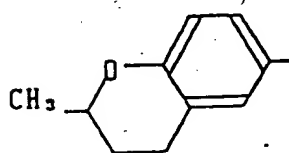
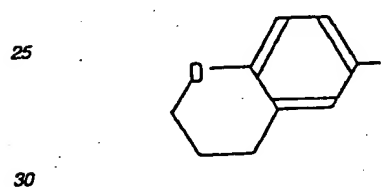
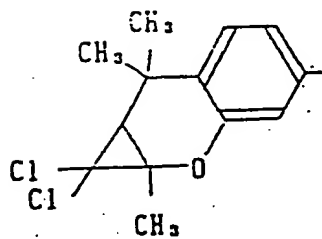
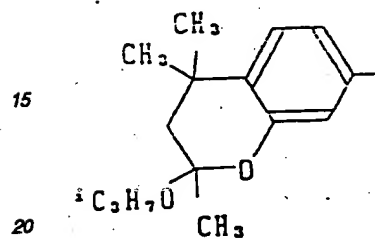
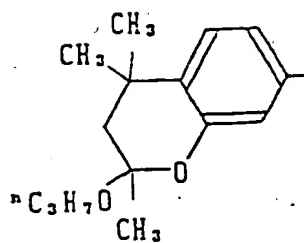
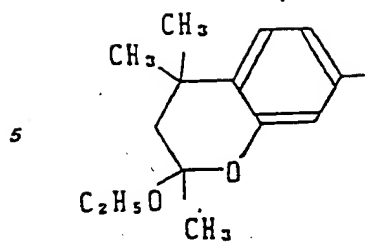
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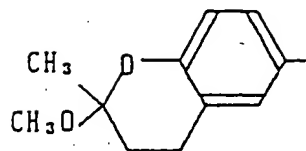
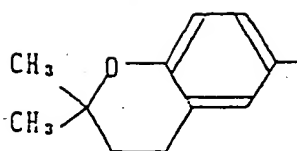
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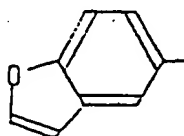
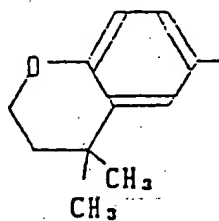
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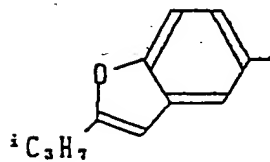
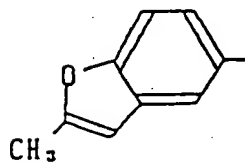
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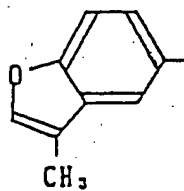
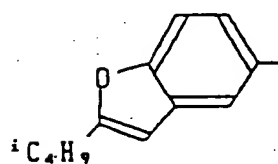
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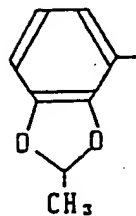
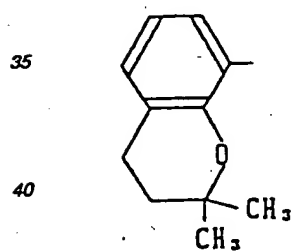
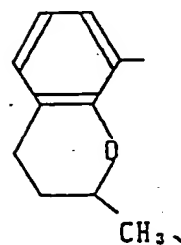
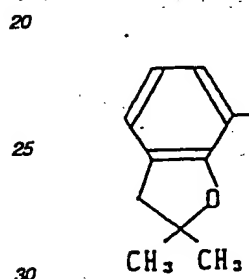
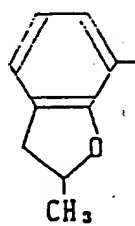
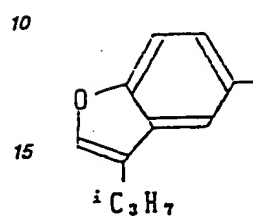
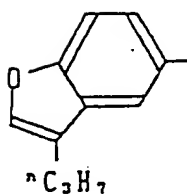
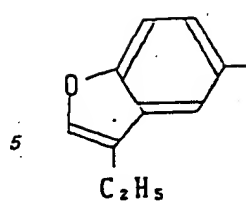
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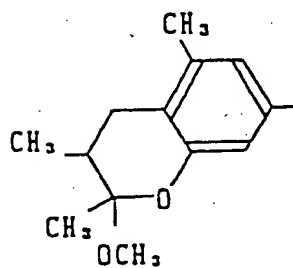
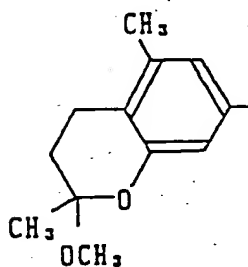
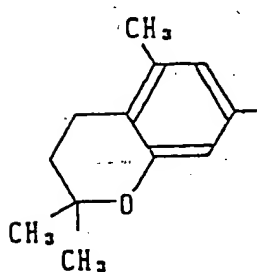
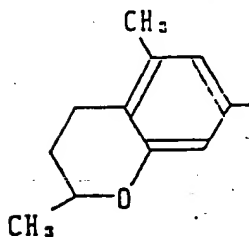
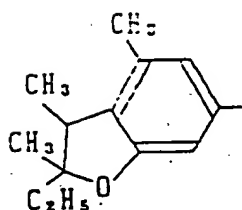
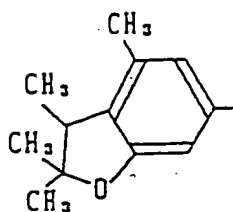
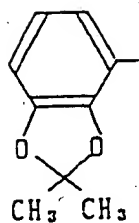
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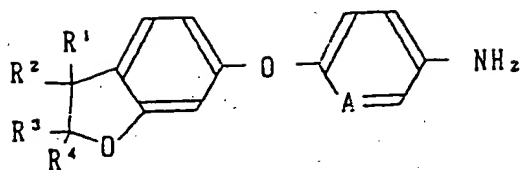
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Preferred examples of the aromatic amine derivatives of the present invention are shown in Tables 1 through 11. Particularly preferred examples of the aromatic amine derivatives of the present invention are compounds shown in Tables 1, 3, 4, 5, 6, 8, 9, 10 and 11.

Table 1



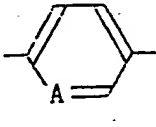
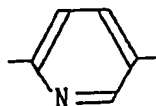
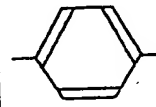
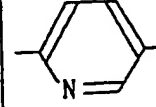
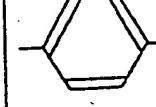
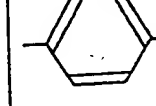
Compound No.	R^1	R^2	R^3	R^4	
1	CH_3	H	H	H	
2	CH_3	H	H	H	
3	CH_3	H	CH_3	CH_3	
4	CH_3	H	CH_3	CH_3	
5	H	H	H	H	

Table 1 (contn'd)

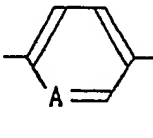
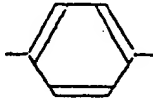
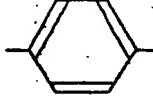
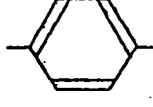
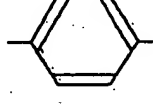
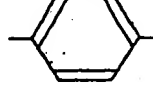
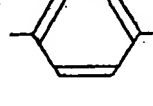
Compound No.	R ¹	R ²	R ³	R ⁴	
6	C ₂ H ₅	H	H	H	
7	C ₃ H ₇ ^a	H	H	H	
8	CH ₃	H	CH ₃	H	
9	H	H	CH ₃	H	
10	H	H	C ₂ H ₅	H	
11	H	H	C ₃ H ₇ ⁱ	H	

Table 1 (contn'd)

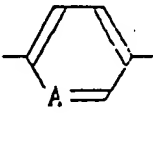
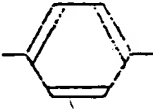
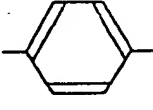
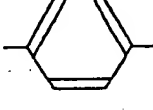
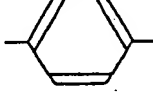
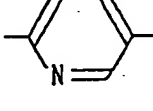
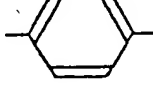
Compound No.	R ¹	R ²	R ³	R ⁴	
1 2	H	H	C ₄ H ₉ ^s	H	
1 3	H	H	CH ₃	CH ₃	
1 4	H	H	CH ₃	C ₂ H ₅	
1 5	H	H	C ₂ H ₅	C ₂ H ₅	
1 6	CH ₃	H	CH ₃	C ₂ H ₅	
1 7	CH ₃	H	CH ₃	C ₂ H ₅	

Table 1 (contn'd)

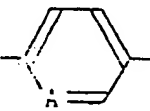
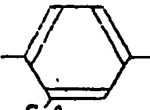
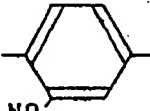
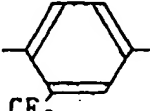
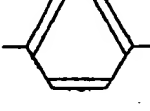
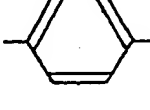
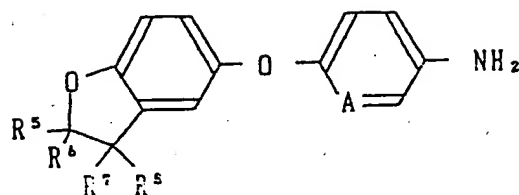
Compound No.	R ¹	R ²	R ³	R ⁴	
1 8	CH ₃	H	CH ₃	C ₂ H ₅	 C ₂ H ₅
1 9	CH ₃	H	CH ₃	C ₂ H ₅	 NO ₂
2 0	CH ₃	H	CH ₃	C ₂ H ₅	 CF ₃
2 1	C ₂ H ₅	H	CH ₃	CH ₃	
2 2	H	-(CH ₂) ₄ -		CH ₃	

Table 2



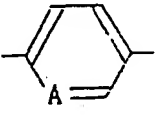
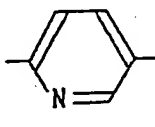
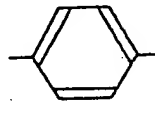
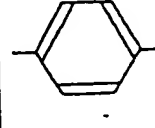
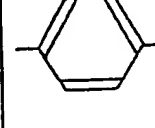
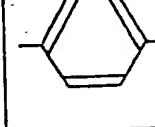
Compound No.	R ⁵	R ⁶	R ⁷	R ⁸	
2 3	CH ₃	H	H	H	
2 4	CH ₃	H	H	H	
2 5	H	H	CH ₃	H	
2 6	H	H	C ₂ H ₅	H	
2 7	H	H	C ₃ H ₇ ⁿ	H	



Table 2 (contn'd)

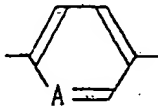
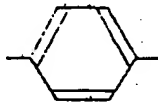
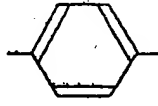
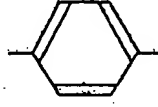
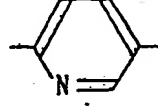
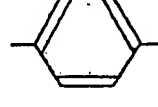
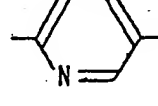
Compound No.	R ⁵	R ⁶	R ⁷	R ⁸	
2 8	H	H	C ₂ H ₅ ¹	H	
2 9	C ₂ H ₅ ¹	H	H	H	
3 0	OCH ₃	H	C ₂ H ₅	H	
3 1	CH ₃	H	CH ₃	H	
3 2	CH ₃	H	CH ₃	H	
3 3	CH ₃	CH ₃	H	H	

Table 2 (contn'd)

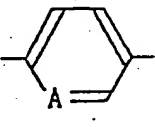
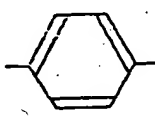
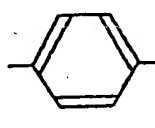
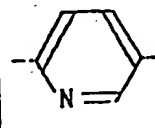
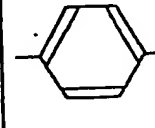
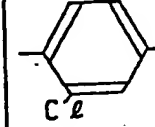
Compound No.	R ⁵	R ⁶	R ⁷	R ⁸	
3 5	H	H	CH ₃	CH ₃	
3 6	OC ₂ H ₅	H	CH ₃	H	
3 7	OCH ₃	H	CH ₃	CH ₃	
3 8	OCH ₃	H	CH ₃	CH ₃	
3 9	OCH ₃	H	CH ₃	CH ₃	

Table 2 (contn'd)

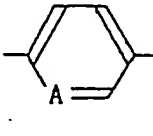
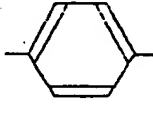
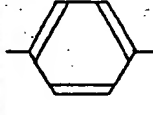
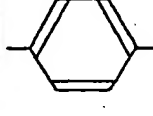
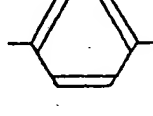
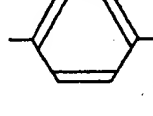
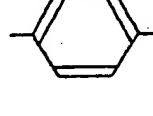
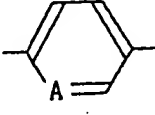
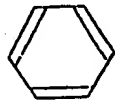
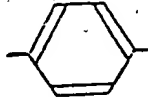
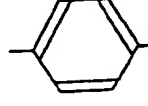
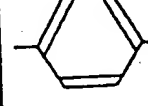
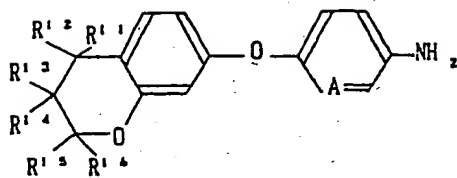
Compound No.	R ⁵	R ⁶	R ⁷	R ⁸	
4 0	OCH ₃	H	CH ₃	C ₂ H ₅	
4 1	OCH ₃	H	C ₂ H ₅	C ₂ H ₅	
4 2	OCH ₃	H	C ₃ H ₇ ⁱ	H	
4 3	OC ₂ H ₅	H	C ₂ H ₅	H	
4 4	OC ₂ H ₅	H	C ₃ H ₇ ⁱ	H	
4 5	OC ₂ H ₅	H	CH ₃	CH ₃	

Table 2 (contn'd)

Compound No.	R ⁵	R ⁶	R ⁷	R ⁸	
4 6	OC ₃ H ₇ ⁱ	H	CH ₃	CH ₃	
4 7	H	-(CH ₂) ₄ -		H	
4 8	H	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}-(\text{CH}_2)_3- \end{array}$		H	
4 9	H	$\begin{array}{c} \text{CH}_3 \\ \\ -(\text{CH}_2)_2-\text{CH}-\text{CH}_2- \end{array}$		H	

0 277 842

Table 4



Compound No.	R^{11}	R^{12}	R^{13}	R^{14}	R^{15}	R^{16}	
6 2	H	H	H	H	H	H	
6 3	CH_3	H	H	H	H	H	
6 4	CH_3	H	H	H	H	H	
6 5	H	H	H	H	CH_3	H	
6 6	H	H	H	H	CH_3	H	

Table 4 (contn'd)

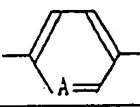
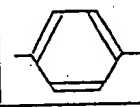
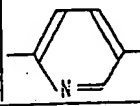
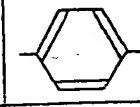
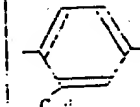
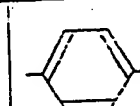
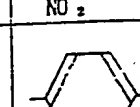
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
6 7	CH ₃	CH ₃	H	H	H	H	
6 8	H	H	H	H	CH ₃	CH ₃	
6 9	H	H	H	H	CH ₃	CH ₃	
7 0	H	H	H	H	CH ₃	CH ₃	
7 1	H	H	H	H	CH ₃	CH ₃	
7 2	H	H	H	H	CH ₃	CH ₃	

Table 4 (contn'd)

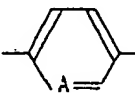
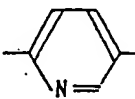
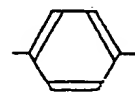
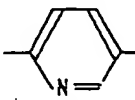
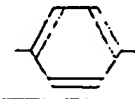
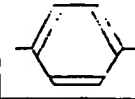
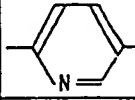
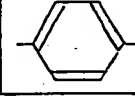
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
7 3	CH ₃	CH ₃	H	H	CH ₃	H	
7 4	CH ₃	CH ₃	H	H	CH ₃	H	
7 5	CH ₃	H	H	H	CH ₃	CH ₃	
7 6	CH ₃	H	H	H	CH ₃	CH ₃	
7 7	OCH ₃	H	H	H	CH ₃	CH ₃	
7 8	CH ₃	CH ₃	H	H	CH ₃	OCH ₃	
7 9	CH ₃	CH ₃	H	H	CH ₃	OCH ₃	

Table 4 (cont'n'd)

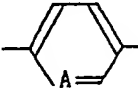
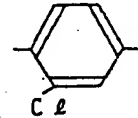
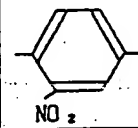
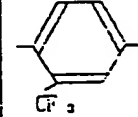
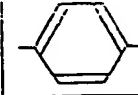
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
8 0	CH ₃	CH ₃	H	H	CH ₃	OCH ₃	
8 1	CH ₃	CH ₃	H	H	CH ₃	OCH ₃	
8 2	CH ₃	CH ₃	H	H	CH ₃	OCH ₃	
8 3	CH ₃	CH ₃	H	H	CH ₃	OC ₂ H ₅	

Table 4 (contn'd)

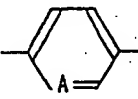
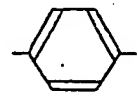
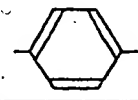
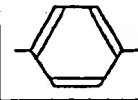
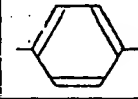
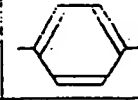
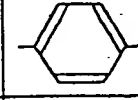
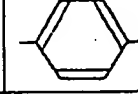
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
8 4	CH ₃	CH ₃	H	H	CH ₃	OC ₂ H ₅ ^h	
8 5	CH ₃	CH ₃	H	H	CH ₃	OC ₂ H ₅ ⁱ	
8 6	OCH ₃	H	H	H	H	H	
8 7	H	H	H	H	C ₂ H ₅	H	
8 8	H	H	H	H	C ₃ H ₇ ⁱ	H	
8 9	H	H	H	H	OCH ₃	H	
9 0	H	H	H	H	OC ₂ H ₅	H	

Table 4 (contn'd)

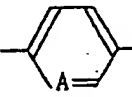
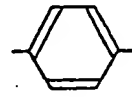
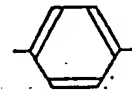
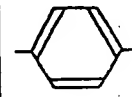
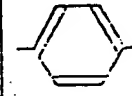
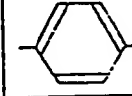
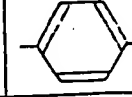
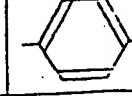
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
9 1	C ₂ H ₅	H	H	H	H	H	
9 2	CH ₃	H	CH ₃	H	H	H	
9 3	CH ₃	H	H	H	CH ₃	H	
9 4	CH ₃	H	H	H	OCH ₃	H	
9 5	CH ₃	H	H	H	OC ₂ H ₅	H	
9 6	OCH ₃	H	H	H	CH ₃	H	
9 7	OCH ₃	H	H	H	C ₂ H ₅	H	



Table 4 (contn'd)

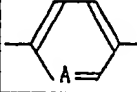
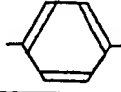
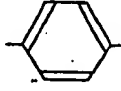
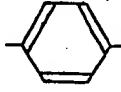
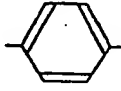
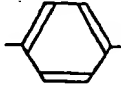
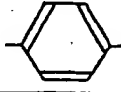
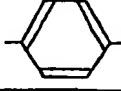
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
9 8	H	H	CH ₃	H	CH ₃	H	
9 9	H	H	CH ₃	H	C ₂ H ₅	H	
1 0 0	H	H	H	H	CH ₃	C ₂ H ₅	
1 0 1	H	H	H	H	CH ₃	C ₃ H ₇ ^a	
1 0 2	H	H	H	H	CH ₃	C ₃ H ₇ ^d	
1 0 3	H	H	H	H	C ₂ H ₅	C ₂ H ₅	
1 0 4	H	H	H	H	C ₂ H ₅	C ₃ H ₇ ^a	

Table 4 (contn'd)

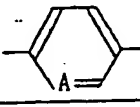
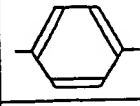
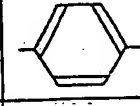
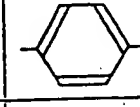
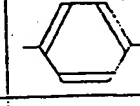
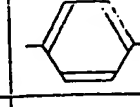
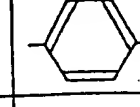
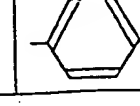
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
1 0 5	H	H	H	H	-(CH ₂) ₅ -		
1 0 6	H	H	H	H	CH ₃	OCH ₃	
1 0 7	H	H	H	H	CH ₃	OC ₂ H ₅	
1 0 8	H	H	H	H	CH ₃	OC ₃ H ₇ ⁱ	
1 0 9	H	H	H	H	C ₂ H ₅	OCH ₃	
1 1 0	CH ₃	H	H	H	CH ₃	OCH ₃	
1 1 1	CH ₃	H	H	H	C ₂ H ₅	OCH ₃	

Table 4 (contn'd)

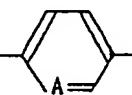
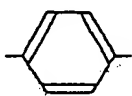
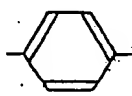
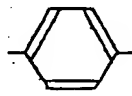
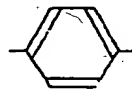
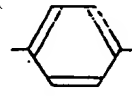
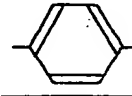
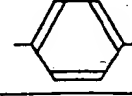
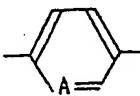
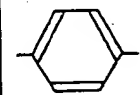
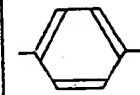
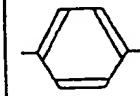

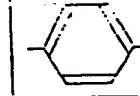
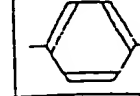
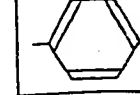
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
1 1 2	OCH ₃	H	CH ₃	H	CH ₃	H	
1 1 3	H	H	CH ₃	H	CH ₃	CH ₃	
1 1 4	H	H	CH ₃	H	CH ₃	OCH ₃	
1 1 5	OCH ₃	H	H	H	CH ₃	C ₂ H ₅	
1 1 6	OCH ₃	H	H	H	CH ₃	C ₃ H ₇ ^d	
1 1 7	OCH ₃	H	H	H	C ₂ H ₅	C ₂ H ₅	
1 1 8	OCH ₃	H	H	H	C ₂ H ₅	C ₃ H ₇ ⁿ	

Table 4 (contn'd)

Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
1 1 9		-O(CH ₂) ₂ O-	H	H	CH ₃	H	
1 2 0		-O(CH ₂) ₂ O-	H	H	C ₂ H ₅	H	
1 2 1		-O(CH ₂) ₂ O-	H	H	C ₃ H ₇ ¹	H	
1 2 2		-O(CH ₂) ₂ O-	CH ₃	H	CH ₃	H	
1 2 3		-O(CH ₂) ₂ O-	H	H	CH ₃	CH ₃	
1 2 4		-O(CH ₂) ₂ O-	H	H	CH ₃	C ₂ H ₅	
1 2 5		-O(CH ₂) ₂ O-	H	H	CH ₃	C ₃ H ₇ ¹	



0 277 842

Table 4 (contn'd)

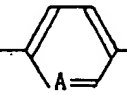
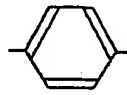
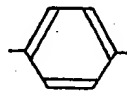
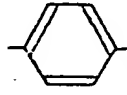
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
1 2 6	$-\text{O}(\text{CH}_2)_2\text{O}-$		H	H	C_2H_5	C_2H_5	
1 2 7	$-\text{O}(\text{CH}_2)_2\text{O}-$		H	H	C_2H_5	$\text{C}_3\text{H}_7^{\text{n}}$	
1 2 8	CH_3	CH_3	H	$-\text{CCl}_2-$		CH_3	

Table 4 (contn'd)

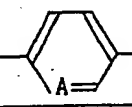
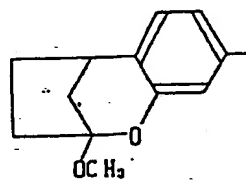
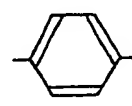
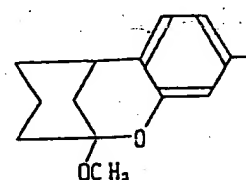
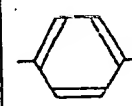
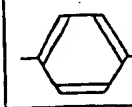
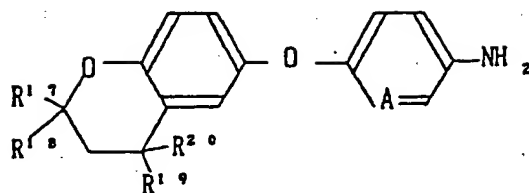
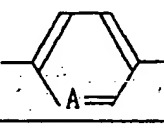
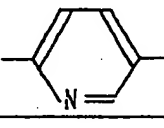
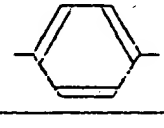
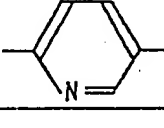
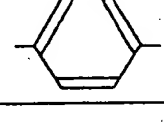
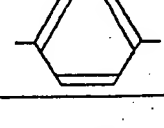
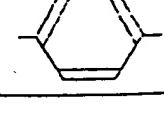
Compound No.	R ¹¹	R ¹²	R ¹³	R ¹⁴	R ¹⁵	R ¹⁶	
1 2 9							
1 3 0							
1 3 1	CH ₃	CH ₃	H	H	CH ₃	OH	

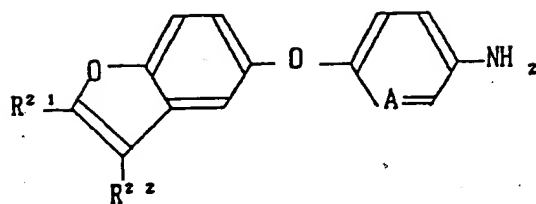
Table 5



Compound No.	R ¹⁷	R ¹⁸	R ¹⁹	R ²⁰	
1 3 2	CH ₃	H	H	H	
1 3 3	CH ₃	H	H	H	
1 3 4	CH ₃	CH ₃	H	H	
1 3 5	CH ₃	CH ₃	H	H	
1 3 6	H	H	CH ₃	CH ₃	
1 3 7	CH ₃	OCH ₃	H	H	

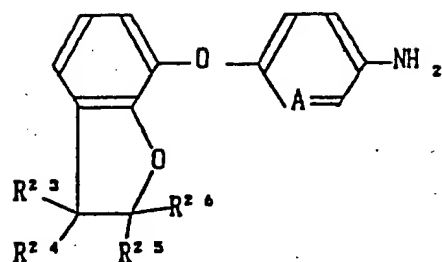
0 277 842

Table 6



Compound No.	R^{21}	R^{22}	
1 3 8	$C_3H_7^i$	H	
1 3 9	$C_4H_9^i$	H	
1 4 0	H	C_2H_5	
1 4 1	H	$C_3H_7^n$	
1 4 2	H	$C_3H_7^i$	

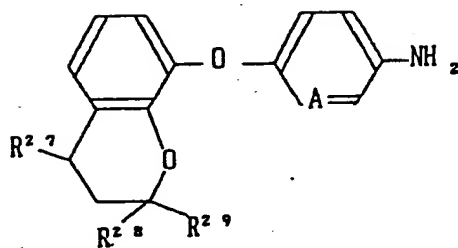
Table 7

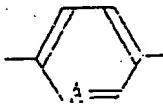
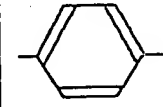


Compound No.	R ²³	R ²⁴	R ²⁵	R ²⁶	
1 4 2	H	H	CH ₂	H	
1 4 4	H	H	CH ₃	H	

0 277 842

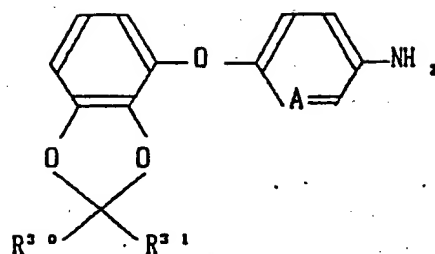
Table 8



Compound No.	R^{27}	R^{28}	R^{29}	
1 4 6	H	CH_3	CH_3	

0 277 842

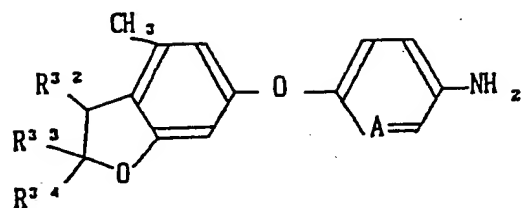
Table 9



Compound No.	R ³⁰	R ³¹	
1 4 7	CH ₃	CH ₃	

0 277 842

Table 1 0



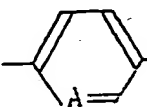
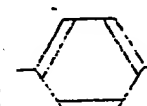
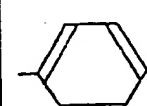
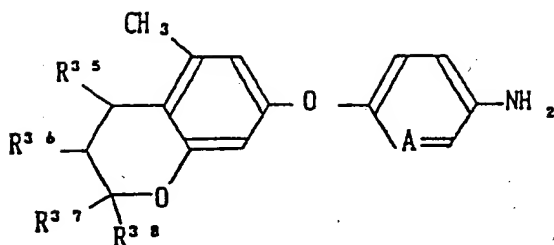
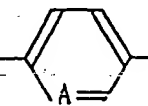
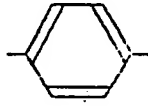
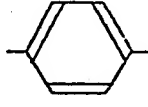
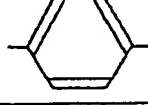
Compound No.	R ³²	R ³³	R ³⁴	
1 4 8	CH ₃	CH ₃	CH ₃	
1 4 9	CH ₃	CH ₃	C ₂ H ₅	

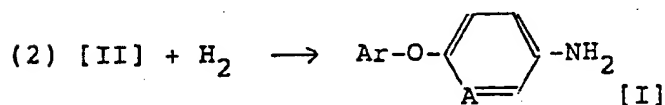
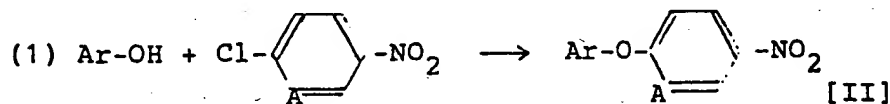
Table 1 1



Compound No.	R ^{3 5}	R ^{3 6}	R ^{3 7}	R ^{3 8}	
1 5 0	H	H	CH ₃	CH ₃	
1 5 1	H	H	OCH ₃	CH ₃	
1 5 2	H	CH ₃	OCH ₃	CH ₃	

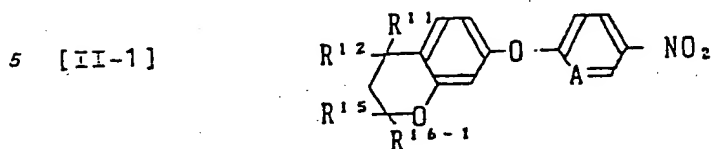
Preparation

The aromatic amine derivatives of the present invention may be prepared through a series of reactions as shown by the following formulae (1) and (2).

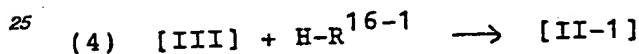
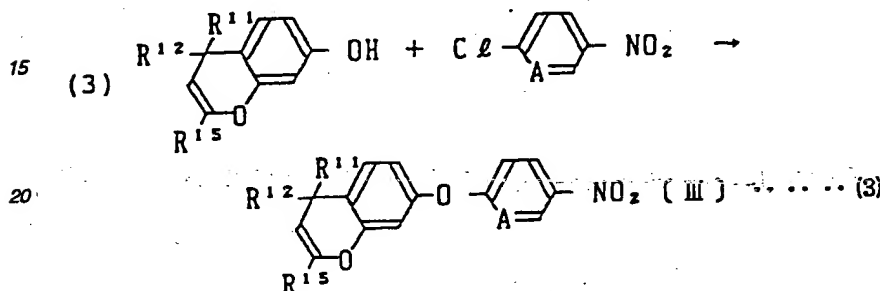


The reaction of formula (1) may be carried out by agitating the reagents in an aromatic hydrocarbon such as benzene, toluene, and xylene, an aprotic polar solvent such as N,N-dimethylformamide and 1-methyl-2-pyrrolidone, or a mixture thereof in the presence of a base such as NaOH, KOH, Na₂CO₃, K₂CO₃, NaH at a temperature of from 20°C to 150°C. The reaction of formula (2) may proceed in a solvent inert to the reaction, for example, benzene, toluene, xylene, methanol, ethanol and ethyl acetate, in the presence of an ordinary reducing catalyst such as Raney nickel catalysts and palladium-carrying carbon under atmospheric pressure to a hydrogen pressure of 20 g/cm² at a temperature of from 20°C to 100°C.

Among the compounds of general formula [II], those compounds represented by general formula [II-1]:

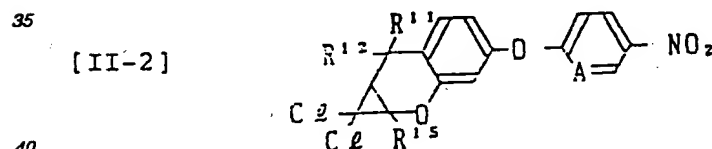


10 wherein R¹¹, R¹², R¹³ and A are as defined above, R¹⁶⁻¹ is a lower alkoxy or hydroxyl radical can be produced not only by the reaction of formula (1), but also by a series of reactions as shown by formulae (3) and (4).

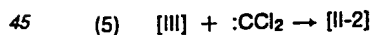


30 The reaction of formula (3) may proceed under the same conditions as described for the reaction of formula (1). The reaction of formula (4) may be carried out without solvent or in an inert solvent such as acetone, dioxane, benzene and toluene in the presence of an acid catalyst such as HCl, H₂SO₄ and Amberlist-15 by heating to a temperature of from 40°C to 120°C.

Among the compounds of general formula [II], those compounds represented by general formula [II-2]:



wherein R¹¹, R¹², R¹⁵ and A are as defined above can be produced not only by the reaction of formula (1), but also by reaction as shown by formula (5).



The reaction of formula (5) can be carried out by agitating a mixture of compound [III], chloroform, and NaOH or KOH without solvent or in an aqueous medium in the presence of a quaternary ammonium salt such as benzyltrimethyl ammonium chloride.

50 At the end of reaction, the end product can be recovered by a conventional method as shown in the following examples.

For typical ones of compounds Ar-OH used in the above preparation procedure, their typical synthesis is exemplified in Table 12 of Japanese Patent Application No. 61-177858 (WO 87/00840). Those compounds which are not exemplified in this Application may also be synthesized by a similar procedure.

EXAMPLES

Examples of the aromatic amine derivatives of the present invention are presented below by way of illustration and not by way of limitation.

60 Reference 1

Synthesis of 2-(3-methyl-2,3-dihydro-6-benzofuryloxy)-5-nitropyridine

65 A 50-ml two-necked round-bottomed flask equipped with a dropping funnel was charged with 0.64 grams of sodium hydride and washed twice with n-hexane. To the flask were added dropwise 2.0 grams of 3-methyl-2,3-dihydro-6-benzofuranol and 10 ml of dimethylformamide at room temperature. After evolution of

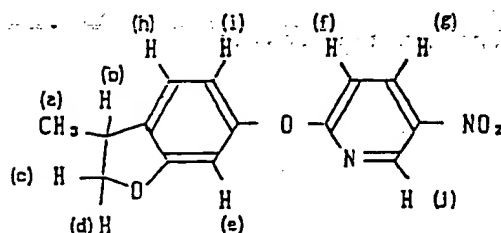
hydrogen ceased, 2.1 grams of 2-chloro-5-nitropyridine in 10 ml of dimethylformamide was added dropwise. The mixture was agitated for 3 hours at room temperature. After water was added to the reaction mixture, the product was extracted with ethyl acetate, washed with water, and then dried over anhydrous magnesium sulfate. The extracting solvent was distilled off to leave a residue, which was purified by chromatography through a silica gel column using a 4/1 n-hexane/ethyl acetate mixture, obtaining 3.0 grams of brown crystals (yield 83%).

Melting point 99.0-99.5°C

IR spectrum (KBr disk; cm^{-1})

3120, 3020, 2950, 1605, 1585, 1515, 1420, 1340, 1240, 998

$^1\text{H-NMR}$ spectrum (CDCl_3 solution; ppm)



57	
(a)	1.38 (3H, d, J= 9.0Hz)
(b)	3.60 (1H, m)
(c)	4.18 (1H, t, J= 8.1Hz)
(d)	4.78 (1H, t, J= 8.1Hz)
(e)	6.63 (1H, d, J= 3.6Hz)
(f)	7.05 (1H, d, J= 9.0Hz)
(g)	7.50 (1H, d, J= 3.6 and 9.0Hz)
(h)	7.63 (1H, d, J= 7.2Hz)
(i)	7.68 (1H, dd, J= 3.6 and 7.2Hz)
(j)	8.10 (1H, d, J= 3.6Hz)

Reference 2

Synthesis of 4-(3-methyl-2,3-dihydro-6-benzofuryloxy)nitrobenzene

A 50-ml two-necked round-bottomed flask equipped with a Dean-Stark apparatus and a condenser was charged with 2.0 grams of 3-methyl-2,3-dihydro-6-benzofuranol, 2.1 grams of 4-chloronitrobenzene, 1.1 grams of 85% potassium hydroxide, 5.0 ml of toluene, and 5.0 ml of dimethylformamide. The mixture was agitated for 2 1/2 hours at 140°C while removing water formed. The reaction mixture was allowed to cool and then combined with water. The product was extracted with ethyl acetate, washed with water, and then dried over anhydrous magnesium sulfate. The extracting solvent was distilled off to leave a residue which was purified by chromatography through a silica gel column using a 4/1 n-hexane/ethyl acetate mixture, obtaining 3.1 grams of pale green crystals (yield 86%).

Melting point 90-91°C

IR spectrum (KBr disk; cm^{-1})

3050, 2960, 1603, 1575, 1420, 1350, 1271, 1237, 1142, 997

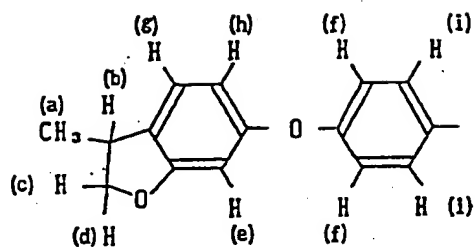
$^1\text{H-NMR}$ spectrum (CDCl_3 solution; ppm)

5

10

15

20



(a) 1.36 (3H, d, J= 7.2Hz)

(b) 3.58 (1H, m)

(c) 4.18 (1H, t, J= 9.0Hz)

(d) 4.78 (1H, t, J= 9.0Hz)

(e) 6.55 (1H, d, J= 2.7Hz)

(f) 7.05 (2H, d, J= 9.0Hz)

(g) 7.18 (2H, d, J= 9.0Hz)

(h) 7.60 (1H, d, J= 7.2 and 9.0Hz)

(i) 8.22 (2H, d, J= 9.0Hz)

25 Example 1Compound No. 1: 2-(3-methyl-2,3-dihydro-6-benzofuryloxy)-5-aminopyridine

In 20 ml of ethyl acetate was dissolved 2.0 grams of 2-(3-methyl-2,3-dihydro-6-benzofuryloxy)-5-nitropyridine. The solution was catalytically reduced in the presence of 0.2 grams of 5% palladium-carrying carbon at room temperature. After absorption of hydrogen ceased, the catalyst was filtered off and the filtrate was concentrated. The concentrate was purified by chromatography through a silica gel column using ethyl acetate solvent, obtaining 1.7 grams of the end product in the form of colorless liquid (yield 97%).

Mass spectrum

m/z 242 (molecular ion peak)

35 IR spectrum (neat; cm⁻¹)

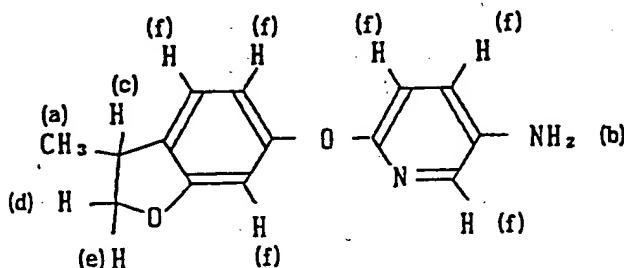
3400, 3050, 2950, 1602, 1357, 1271, 1235, 1130

¹H-NMR spectrum (CDCl₃ solution; ppm)

40

45

50



(a) 1.32 (3H, d, J= 7.2Hz)

(b) 3.28 (2H, brs)

(c) 3.24 ~ 3.72 (1H, m)

(d) 4.09 (1H, t, J= 7.2Hz)

(e) 4.72 (1H, t, J= 7.2Hz)

(f) 6.44 ~ 7.84 (6H, m)

60 Example 2Compound No. 2: 4-(3-methyl-2,3-dihydro-6-benzofuryloxy)aniline

The procedure of Example 1 was repeated except that the 2-(3-methyl-2,3-dihydro-6-benzofuryloxy)-5-nitropyridine was replaced by 4-(3-methyl-2,3-dihydro-6-benzofuryloxy)nitrobenzene. The reaction mixture was worked up in the same manner as in Example 1, obtaining the end product in the form of brown liquid (yield

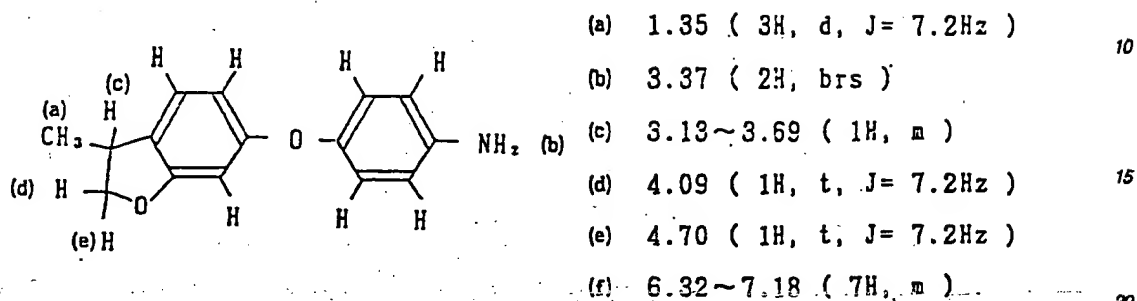
98%).

Mass spectrum

m/z 241 (molecular ion peak)

IR spectrum (neat; cm^{-1})

3350, 3050, 2970, 1601, 1357, 1270, 1236, 1132

 ^1H -NMR spectrum (CDCl_3 solution; ppm)

Compound Nos. 3 to 152 were synthesized by the same procedure as in Example 1. The results are summarized in Tabel 12. The yield was at least 95% for all the compounds.

Table 12

Compound No.	As-produced	Spectral analysis
3	viscous liquid	NMR : 1.20(3H,d, J = 8.1), 1.28(3H,s), 1.47(3H,s), 3.07(1H,q, J = 8.1), 3.35(2H,brs), 6.24~8.00(6H,m).
4	viscous liquid	NMR : 1.19(3H,d, J = 9.0), 1.45(3H,s), 3.10(1H,q, J = 9.0), 3.38(2H,brs), 6.20~7.10(7H,m).
5	viscous liquid	NMR : 3.15(2H,t, J = 7.2), 3.40(2H,brs), 4.60(2H,t, J = 7.2), 6.20~7.40(7H,m).
6	viscous liquid	NMR : 0.96(3H,t, J = 7.2), 1.70(2H,q, J = 7.2), 3.30(1H,m), 3.42(2H,brs), 4.24(1H,t, J = 9.0), 4.65(1H,t, J = 9.0), 6.30~7.50(7H,m).
7	viscous liquid	IR : 3350 (ν_{OH}), 3100, 2980, 1610, 1270, 1230.
8	viscous liquid	
9	viscous liquid	NMR : 1.46(3H,d, J = 7.2), 2.74(1H,dd, J = 8.0, 15.0), 3.27(1H,dd, J = 8.0, 15.0), 3.52(2H,brs), 4.94(1H,m), 6.28~7.42(7H,m).
10	viscous liquid	NMR : 1.04(3H,t, J = 7.2), 1.76(2H,m), 2.78(1H,dd, J = 8.0, 15.0), 3.22(1H,dd, J = 8.0, 15.0), 3.55(2H,brs), 6.20~7.10(7H,m).
11	viscous liquid	NMR : 0.98(3H,d, J = 7.2), 1.06(3H,d, J = 7.2), 1.89(1H,m), 2.85(1H,dd, J = 8.0, 15.0), 3.14(1H,dd, J = 8.0, 15.0), 3.48(2H,brs), 4.54(1H,m), 6.35~7.20(7H,m).
12	viscous liquid	NMR : 0.93(3H,t, J = 7.2), 1.00(3H,d, J = 7.2), 1.61(3H,m), 2.70~3.30(2H,m), 3.42(2H,brs), 6.35~7.20(7H,m).
13	m.p. 86~87°C	

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
1 4	viscous liquid	NMR : 0.95(3H,t,J = 7.0), 1.40(3H,s), 1.74(2H,q,J = 7.0), 2.95(2H,s), 3.42(2H,brs), 6.30~7.40(7H,m).
1 5	viscous liquid	NMR : 0.91(6H,t,J = 7.0), 1.70(4H,q,J = 7.0), 2.95(2H,s), 3.46(2H,brs), 6.30~7.20(7H,m).
1 6	viscous liquid	NMR : 0.90(3H,t,J = 7.2), 1.14(3H,d,J = 6.3), 1.17(3H,s), 1.70(2H,q,J = 7.2), 3.08(1H,q,J = 6.3), 3.30(2H,brs), 6.25~7.60(6H,m).
1 7	viscous liquid	NMR : 0.98(3H,t,J = 7.2), 1.20(3H,d,J = 6.3), 1.24(3H,s), 1.75(2H,q,J = 7.2), 3.10(1H,q,J = 6.3), 3.45(2H,brs), 6.30~7.20(7H,m).
1 8	viscous liquid	NMR : 0.99(3H,t,J = 7.2), 1.22(3H,d,J = 6.3), 1.24(3H,s), 1.78(2H,q,J = 7.2), 3.18(1H,d,J = 6.3), 3.52(2H,brs), 6.28~7.50(7H,m).
1 9	viscous liquid	IR : 3400, 3320 (ν_{NH}).
2 0	viscous liquid	IR : 3410, 3310 (ν_{NH}).
2 1	viscous liquid	NMR : 1.26(3H,t,J = 7.2), 1.34(3H,s), 1.46(3H,s), 1.63(2H,m), 2.84(1H,t,J = 9.0), 3.36(2H,brs), 6.18~7.16(7H,m).
2 2	viscous liquid	
2 3	viscous liquid	NMR : 1.49(3H,d,J = 6.3), 2.80~3.40(2H,m), 3.55(2H,brs), 4.90(1H,m), 6.24~7.62(6H,m).
2 4	m.p. 101~102 °C	
2 5	viscous liquid	NMR : 1.29(3H,d,J = 6.9), 3.52(3H,m), 4.12(1H,t,J = 9.0), 4.71(1H,t,J = 9.0), 6.20~7.15(7H,m).

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
2 6	viscous liquid	NMR : 0.94(3H,t,J = 7.2), 1.70(2H,q,J = 7.2), 3.44(3H,m), 4.21(1H,dd,J = 7.2, 9.0), 4.63(1H,t,J = 9.0), 6.15~7.50(7H,m).
2 7	viscous liquid	NMR : 0.96(3H,t,J = 7.0), 1.24~1.70(4H,m), 3.10(1H,m), 3.42(2H,brs), 4.21(1H,dd,J = 7.2, 9.0), 4.66(1H,t,J = 9.0), 6.34~7.26(7H,m).
2 8	viscous liquid	
2 9	viscous liquid	
3 0	viscous liquid	NMR : 0.97(3H,t,J = 7.2), 1.36~1.90(2H,m), 2.90~3.20(1H,m), 3.50(2H,brs), 3.53(3H,s), 5.26(3H,d,J = 2.7), 6.52~7.36(7H,m).
3 1	viscous liquid	
3 2	m.p. 89.5~90.5°C	
3 3	viscous liquid	
3 5	m.p. 94.5~95.5°C	
3 6	viscous liquid	
3 7	viscous liquid	NMR : 1.27(3H,s), 1.29(3H,s), 3.30(2H,brs), 3.56(3H,s), 5.13(1H,s), 6.50~7.00(6H,m).
3 8	viscous liquid	NMR : 1.25(3H,s), 1.28(3H,s), 3.30(2H,brs), 3.56(3H,s), 5.11(1H,s), 6.4H~7.00(7H,m).
3 9	viscous liquid	NMR : 1.24(3H,s), 1.28(3H,s), 3.34(3H,s), 3.60(2H,brs), 5.10(1H,s), 6.40~6.90(6H,m).

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
4 0	viscous liquid	
4 1	viscous liquid	
4 2	viscous liquid	NMR : 0.90(3H,d,J =6.4), 0.94(3H,d,J =6.4), 1.72~2.00(1H,m), 2.50~2.70(1H,m), 3.34(2H,brs), 5.32(3H,d,J =2.1), 6.40~7.20(7H,m).
4 3	viscous liquid	NMR : 0.96(3H,t,J =7.7), 1.23(3H,t,J =7.1), 1.40~1.84(2H,m), 3.01~3.16(1H,m), 3.52~4.00(4H,m), 5.38(1H,d,J =2.1), 6.41~7.18(7H,m).
4 4	viscous liquid	NMR : 0.88(3H,d,J =6.4), 0.92(3H,d,J =6.4), 1.24(3H,t,J =7.1), 1.80~2.12(1H,m), 3.02~3.12(1H,m), 3.52~4.06(4H,m), 5.44(1H,d,J =1.5), 6.40~7.18(4H,m).
4 5	viscous liquid	
4 6	viscous liquid	
4 7	viscous liquid	NMR : 1.30~2.16(8H,m), 3.13~3.36(1H,m), 3.52(2H,brs), 4.64~4.88(1H,m), 6.32~7.41(7H,m).
4 8	viscous liquid	IR : 3400 (ν_{OH}), 3040, 2960, 1570, 1270, 1120.
4 9	viscous liquid	
5 0	viscous liquid	NMR : 3.48(2H,brs), 5.89(2H,s), 6.20~6.90(7H,m)
5 1	viscous liquid	NMR : 1.01(3H,t,J =7.2), 1.61(3H,s), 1.95(2H,q,J =7.2), 3.40(2H,brs), 6.20~7.10(7H,m).
5 2	viscous liquid	
5 3	viscous liquid	NMR : 1.68(6H,s), 3.45(2H,brs), 6.20~7.10(7H,m).

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
5 4	viscous liquid	NMR : 1.78(3H,s), 3.31(3H,s), 3.55(2H,brs), 6.30~7.00(7H,m).
5 5	viscous liquid	NMR : 1.21(3H,t,J = 7.2), 1.80(3H,s), 3.32(2H,brs), 3.61(2H,q,J = 7.2), 6.30~7.08(7H,m).
5 6	viscous liquid	NMR : 1.02(3H,t,J = 7.2), 1.21(3H,t,J = 7.2), 2.06(2H,q,J = 7.2), 3.56(2H,q,J = 7.2), 3.60(2H,brs), 6.30~7.60(7H,m).
5 7	viscous liquid	
5 8	viscous liquid	
5 9	viscous liquid	IR : 3400 (ν_{OH}), 3060, 2970, 1603.
6 0	viscous liquid	
6 1	viscous liquid	IR : 3420 (ν_{OH}), 3040, 2970, 1603, 1275.
6 2	viscous liquid	
6 3	viscous liquid	IR : 3400 (ν_{OH}), 3060, 2855, 1605, 1275, 1238.
6 4	m.p. 109~110 °C	
6 5	viscous liquid	NMR : 1.38(3H,d,J = 7.2), 1.60~2.00(2H,m), 2.64~2.94(2H,m), 3.37(2H,m), 6.40~7.80(6H,m).
6 6	viscous liquid	NMR : 1.38(3H,d,J = 9.0), 1.80(2H,m), 2.72(2H,m), 2.64(2H,brs), 4.16(1H,m), 6.40~7.80(6H,m).
6 7	m.p. 115.5~116.5 °C	
6 8	m.p. 93~94 °C	NMR : 1.30(6H,s), 1.76(2H,t,J = 7.2), 2.72(2H,t,J = 7.2), 3.38(2H,brs), 6.40~7.80(6H,m).

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
6 9	viscous liquid	NMR : 1.30(6H,s), 1.77(2H,t,J = 7.2), 2.72(2H,t,J = 7.2), 3.44(2H,brs), 6.20~7.18(7H,m).
7 0	viscous liquid	NMR : 1.32(6H,s), 1.78(2H,t,J = 7.2), 2.72(2H,t,J = 7.2), 3.64(2H,brs), 6.20~7.10(6H,m).
7 1	viscous liquid	IR : 3420 (ν_{NH}), 3040, 2970, 1605, 1535, 1370.
7 2	viscous liquid	
7 3	viscous liquid	NMR : 1.29(3H,s), 1.32(3H,d,J = 7.2), 1.62(1H,s), 1.68(1H,s), 3.28(2H,brs), 4.16(1H,q,J = 7.2), 6.40~7.80(6H,m).
7 4	viscous liquid	
7 5	viscous liquid	IR : 3380 (ν_{NH}), 3180, 3040, 2960, 1605, 1275.
7 6	viscous liquid	IR : 3410 (ν_{NH}), 3060, 2970, 1610, 1270, 1235, 1140.
7 7	viscous liquid	NMR : 1.32(3H,s), 1.41(3H,s), 1.99(1H,d,J = 7.2), 2.03(1H,d,J = 7.2), 3.44(3H,s), 3.50(2H,brs), 4.38(1H,t,J = 7.2), 6.20~7.40(7H,m).
7 8	m.p. 104.5~105.5 °C	
7 9	viscous liquid	NMR : 1.26(3H,s), 1.41(3H,s), 1.49(3H,s), 1.81(1H,d,J = 14.0), 1.95(1H,d,J = 14.0), 2.65(2H,brs), 3.23(3H,s), 6.40~7.30(7H,m).
8 0	viscous liquid	NMR : 1.25(3H,s), 1.41(3H,s), 1.48(3H,s), 1.89(1H,d,J = 14.4), 2.02(1H,d,J = 14.4), 3.21(3H,s), 3.64(2H,brs), 6.20~7.32(7H,m).
8 1	viscous liquid	IR : 3410 (ν_{NH}), 3330(ν_{NH}), 1610, 1524, 1470, 1350, 1265, 1230.



Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
8 2	viscous liquid	
8 3	viscous liquid	NMR : 1.00(3H, t, J = 7.2), 1.26(3H, s), 1.44(3H, s), 1.50(3H, s), 1.88(1H, d, J = 14.0), 1.95(1H, d, J = 14.0), 3.35(2H, brs), 3.55(2H, q, J = 7.2), 6.32~7.30(7H, m).
8 4	viscous liquid	NMR : 0.72(3H, t, J = 7.2), 1.20~1.60(2H, m), 1.28(3H, s), 1.46(3H, s), 1.54(3H, s), 1.84(1H, d, J = 13.5), 2.05(1H, d, J = 13.5), 3.47(4H, m), 6.20 ~ 7.20(7H, m).
8 5	viscous liquid	NMR : 0.84, 1.11(total 6H, d, J = 7.2), 1.25(3H, s), 1.45(3H, s), 1.51(3H, s), 1.74(1H, d, J = 13.5), 1.99(1H, d, J = 13.5), 3.56(2H, brs), 4.12(1H, m), 6.30~7.26(7H, m).
8 6	viscous liquid	NMR : 1.82~2.20(2H, m), 3.43(3H, s), 3.48(2H, brs), 4.10~4.36(3H, m), 6.30~7.35(7H, m).
8 7	viscous liquid	NMR : 1.00(3H, t, J = 7.2), 1.40~2.16(4H, m), 2.50~3.00(2H, m), 3.50(2H, brs), 3.70~4.04(1H, m), 6.20~7.33(7H, m).
8 8	viscous liquid	
8 9	viscous liquid	NMR : 1.90(2H, m), 2.56(2H, m), 3.40(3H, s), 3.52(2H, brs), 5.01(1H, t, J = 1.8), 6.18~7.31(7H, m).
9 0	viscous liquid	
9 1	viscous liquid	NMR : 1.00(3H, t, J = 7.2), 1.80(4H, m), 2.60(1H, m), 3.48(2H, brs), 4.16(2H, t, J = 5.4), 6.10~7.15(7H, m).

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
9 2	viscous liquid	NMR : 0.97(3H,d, J = 7.2), 1.18(3H,d, J = 7.2), 2.00~2.10(1H,m), 2.72~3.04(1H,m), 3.48(2H,brs), 3.78~4.20(2H,m), 6.30~7.10(7H,m).
9 3	viscous liquid	
9 4	viscous liquid	NMR : 1.30, 1.35(total 3H,d, J = 7.2), 1.60~2.28(2H,m), 2.94(1H,m), 3.47, 3.51(total 3H,s), 3.49(2H,brs), 6.30~7.42(7H,m).
9 5	viscous liquid	NMR : 1.00~1.50(6H,m), 1.60~2.28(2H,m), 3.08(1H,m), 3.24~4.08(4H,m), 5.20(1H,dd, J = 3.6, 7.2), 6.32~7.46(7H,m).
9 6	viscous liquid	NMR : 1.40(3H,d, J = 7.2), 1.62~2.44(2H,m), 3.44(3H,s), 3.54(2H,brs), 4.20(1H,m), 4.56(1H,dd, J = 6.3, 10.8), 6.21~7.32(7H,m).
9 7	viscous liquid	
9 8	viscous liquid	NMR : 0.96(3H,d, J = 7.2), 1.26(3H,d, J = 7.2), 2.00~3.08(3H,m), 3.48(2H,m), 4.08~4.18(1H,m), 6.33~7.20(7H,m).
9 9	viscous liquid	NMR : 0.82~1.12(6H,m), 1.20~1.81(3H,m), 2.20~2.80(2H,m), 3.48(2H,brs), 4.10(1H,m), 6.24~7.28(7H,m).
1 0 0	viscous liquid	
1 0 1	viscous liquid	IR : 3420 (ν_{NH}), 3070, 2940, 1570, 1275, 1238.
1 0 2	viscous liquid	IR : 3420 (ν_{NH}), 3050, 2955, 1610, 1570, 1575, 1240.
1 0 3	viscous liquid	

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
1 0 4	m.p. 85~86°C	NMR : 0.89(6H,t,J = 7.2), 1.25~1.67(6H,m), 1.78(2H,t,J = 7.2), 2.68(2H,t,J = 7.2), 3.48(2H,brs), 6.32~7.22(7H,m).
1 0 5	viscous liquid	
1 0 6	viscous liquid	NMR : 1.55(3H,s), 1.64~2.24(2H,m), 2.36~3.04(2H,m), 3.28(2H,brs), 3.30(3H,s), 6.36~7.10(7H,m).
1 0 7	viscous liquid	NMR : 1.04(3H,t,J = 7.2), 1.50(3H,s), 1.70~2.28(2H,m), 2.60~3.24(2H,m), 3.48(2H,brs), 3.62(2H,q,J = 7.2), 6.36~7.40(7H,m).
1 0 8	viscous liquid	NMR : 0.85(3H,t,J = 7.2), 1.14(3H,t,J = 7.2), 1.54(3H,s), 1.66~2.24(2H,m), 2.40~2.80(2H,m), 3.49(2H,brs), 4.22(1H,m), 6.26~7.38(7H,m).
1 0 9	viscous liquid	NMR : 0.95(3H,t,J = 7.2), 1.50~2.20(4H,m), 2.40~3.00(2H,m), 3.24(3H,s), 3.38(2H,brs), 6.36~7.08(7H,m).
1 1 0	viscous liquid	
1 1 1	viscous liquid	
1 1 2	viscous liquid	NMR : 1.08(3H,d,J = 7.2), 1.40(3H,d,J = 7.2), 1.60~2.00(1H,m), 3.31(3H,s), 3.51(2H,brs), 3.80~4.36(2H,m), 6.20~7.40(7H,m).
1 1 3	viscous liquid	NMR : 0.99(3H,d,J = 7.2), 1.14(3H,s), 1.35(3H,s), 1.62~2.10(1H,m), 2.30~2.08(2H,m), 3.47(2H,brs), 6.30~7.12(7H,m).
1 1 4	viscous liquid	NMR : 1.08(3H,d,J = 7.2), 1.49(3H,s), 1.98(1H,m), 2.46~2.76(2H,m), 3.23(3H,s), 3.42(2H,brs), 6.20~7.12(7H,m).

Table 12 (contn'd)

compound No.	As-produced	Spectral analysis
1 1 5	viscous liquid	NMR : 0.94(3H,t,J = 7.2), 1.25 and 1.36(total 3H,s), 1.50~1.76(2H,m), 1.81~2.12(2H,m), 3.44 and 3.46(total 3H,s), 3.54(2H,brs), 4.41(1H,brs), 6.24~7.30(7H,m).
1 1 6	viscous liquid	
1 1 7	viscous liquid	NMR : 0.89(6H,t,J = 7.2), 1.50~2.10(6H,m), 3.44(3H,s), 3.50(2H,brs), 4.37(1H,t,J = 6.3), 6.20~7.40(7H,m).
1 1 8	viscous liquid	NMR : 0.90(6H,t,J = 7.2), 1.10~2.20(8H,m), 3.46(3H,s), 3.52(2H,brs), 4.38(1H,t,J = 7.2), 6.30~7.40(7H,m).
1 1 9	viscous liquid	
1 2 0	viscous liquid	NMR : 1.04(3H,t,J = 7.2), 1.52~2.14(4H,m), 3.42(3H,brs), 3.92~4.40(5H,m), 6.20~7.20(7H,m).
1 2 1	viscous liquid	NMR : 1.00(6H,d,J = 6.3), 1.85~1.94(3H,m), 3.47(2H,brs), 4.04(1H,m), 4.15(4H,m), 6.30~7.32(7H,m).
1 2 2	viscous liquid	NMR : 0.97(3H,d,J = 7.0), 1.38(3H,d,J = 7.0), 2.12(1H,m), 3.50(2H,brs), 4.09~4.35(5H,m), 6.33~7.18(7H,m).
1 2 3	viscous liquid	NMR : 1.42(6H,s), 2.13(2H,s), 3.50(2H,brs), 4.00~4.30(4H,m), 6.24~7.14(7H,m).
1 2 4	viscous liquid	NMR : 0.92(3H,t,J = 7.0), 1.34(3H,s), 1.70(2H,q,J = 7.2), 2.01(1H,d,J = 14.4), 2.20(1H,d,J = 14.4), 3.20(2H,brs), 4.00~4.30(4H,m), 6.30~7.44(7H,m).
1 2 5	viscous liquid	

Table 12 (contn'd)

compound no.	As-produced	Spectral analysis
1 2 6	viscous liquid	NMR : 0.87(6H, t, J = 7.2), 1.68(4H, q, J = 7.2), 2.10(2H, s), 3.42(2H, brs), 4.00~4.30(4H, m), 6.22~7.20(7H, m).
1 2 7	viscous liquid	NMR : 0.80(6H, t, J = 7.2), 1.10~1.50(2H, m), 1.69(4H, q, J = 7.2), 2.09(2H, s), 3.49(2H, brs), 3.90~4.30(4H, m), 6.18~7.10(7H, m).
1 2 8	viscous liquid	NMR : 1.36(3H, s), 1.62(3H, s), 1.68(1H, s), 1.80(3H, s), 3.54(2H, brs), 6.20~7.18(7H, m).
1 2 9	viscous liquid	NMR : 1.80~2.24(6H, m), 3.06(1H, m), 3.53(3H, s), 3.55(2H, brs), 6.32~7.22(7H, m).
1 3 0	viscous liquid	NMR : 1.40~1.92(6H, m), 2.00~2.30(2H, m), 3.18(1H, m), 3.50(2H, brs), 3.76(3H, s), 6.18~7.32(7H, m).
1 3 1	m.p. 140.0~141.0	IR : 3385, 3320 (ν_{NH}), 3040 (ν_{CH}), 1610, 1578, 1490, 1208, 1132, 1162, 990. NMR : 1.31(3H, s), 1.47(3H, s), 1.60(3H, s), 1.82(1H, d, J = 13.5), 2.04(1H, d, J = 13.5), 3.12(2H, brs), 6.35(1H, d, J = 2.7), 6.55(1H, dd, J = 2.7, 9.0), 6.65(2H, d, J = 9.0), 6.89(2H, d, J = 9.0), 7.20(1H, d, J = 9.0).
1 3 2	viscous liquid	NMR : 1.40(3H, d, J = 7.2), 1.80(2H, m), 2.74(2H, m), 3.48(2H, brs), 4.12(1H, m), 6.60~7.84(6H, m).
1 3 3	viscous liquid	NMR : 1.38(2H, d, J = 7.2), 1.80(2H, m), 2.70(2H, m), 3.52(2H, brs), 4.11(1H, m), 6.52~6.96(7H, m).
1 3 4	viscous liquid	NMR : 1.33(6H, s), 1.70(2H, t, J = 7.2), 2.75(2H, t, J = 7.2), 3.25(2H, brs), 6.60~7.80(6H, m).



Table 12 (contn'd)

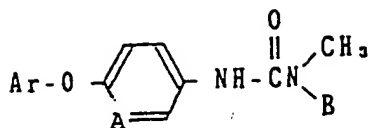
Compound No.	As-produced.	Spectral analysis
1 3 5	viscous liquid	
1 3 6	viscous liquid	
1 3 7	viscous liquid	NMR : 1.55(3H,s), 1.66~2.21(2H,m), 2.32~3.10(2H,m), 3.22(2H,brs), 3.30(3H,s), 6.50~7.00(7H,m).
1 3 8	viscous liquid	NMR : 1.35(6H,d,J = 6.9), 2.98~3.10(1H,m), 3.48(2H,brs), 6.36(1H,s), 6.30~7.32(7H,m).
1 3 9	viscous liquid	NMR : 0.98(3H,d,J = 6.9), 1.02(3H,d,J = 6.9), 1.90~2.28(1H,m), 2.64(2H,dd,J = 2.7, 6.7), 3.47(2H,brs), 6.32(1H,s), 6.34~7.18(7H,m).
1 4 0	viscous liquid	NMR : 1.30(3H,t,J = 7.7), 2.64(2H,q,J = 7.7), 6.32~7.34(8H,m).
1 4 1	viscous liquid	NMR : 0.80~1.04(5H,m), 1.56(2H,t,J = 7.7), 3.50(2H,brs), 6.20~7.40(8H,m).
1 4 2	viscous liquid	NMR : 1.30(6H,d,J = 6.7), 2.90~3.14(1H,m), 3.47(2H,brs), 6.20~7.35(8H,m).
1 4 3	viscous liquid	NMR : 1.42(3H,d,J = 6.3), 2.84(1H,dd,J = 7.2, 14.4), 2.96(1H,dd,J = 7.2, 14.4), 3.56(2H,brs), 4.92(1H,m), 6.20~7.60(6H,m).
1 4 4	viscous liquid	NMR : 1.48(3H,d,J = 6.4), 2.88(1H,dd,J = 7.7, 15.4), 3.38(1H,dd,J = 7.7, 15.4), 3.52(2H,brs), 5.00(1H,m), 6.38~7.92(8H,m).
1 4 6	viscous liquid	NMR : 1.26(6H,s), 1.80(2H,t,J = 7.1), 2.82(2H,t,J = 7.1), 3.52(2H,brs), 6.33~7.10(7H,m).
1 4 7	viscous liquid	

Table 12 (contn'd)

Compound No.	As-produced	Spectral analysis
1 4 8	viscous liquid	NMR : 1.19(3H, d, J = 7.2), 1.37(3H, s), 1.40(3H, s), 2.24(3H, s), 3.10(1H, q, J = 7.2), 3.48(2H, brs), 6.20~7.20(6H, m).
1 4 9	viscous liquid	NMR : 0.92(3H, t, J = 7.2), 1.18(3H, d, J = 6.3), 1.30(3H, s), 1.68(2H, q, J = 7.2), 2.20(3H, s), 3.12(1H, q, J = 6.3), 3.52(2H, brs), 6.30~7.22(6H, m).
1 5 0	viscous liquid	NMR : 1.30(3H, s), 1.82(2H, t, J = 6.7), 2.16(3H, s), 2.60(2H, t, J = 6.7), 3.52(2H, brs), 6.20~7.12(6H, m).
1 5 1	viscous liquid	
1 5 2	viscous liquid	NMR : 1.16(3H, d, J = 7.2), 1.52(3H, s), 1.80~2.12(1H, m), 2.22(3H, s), 2.44(2H, d, J = 9.0), 3.24(3H, s), 3.48(2H, brs), 6.24~7.42(6H, m).

The aromatic amine derivatives of the present invention are useful as intermediates for herbicides. More particularly, compounds of general formula [IV]:

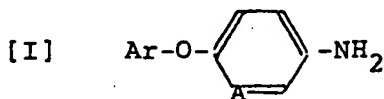




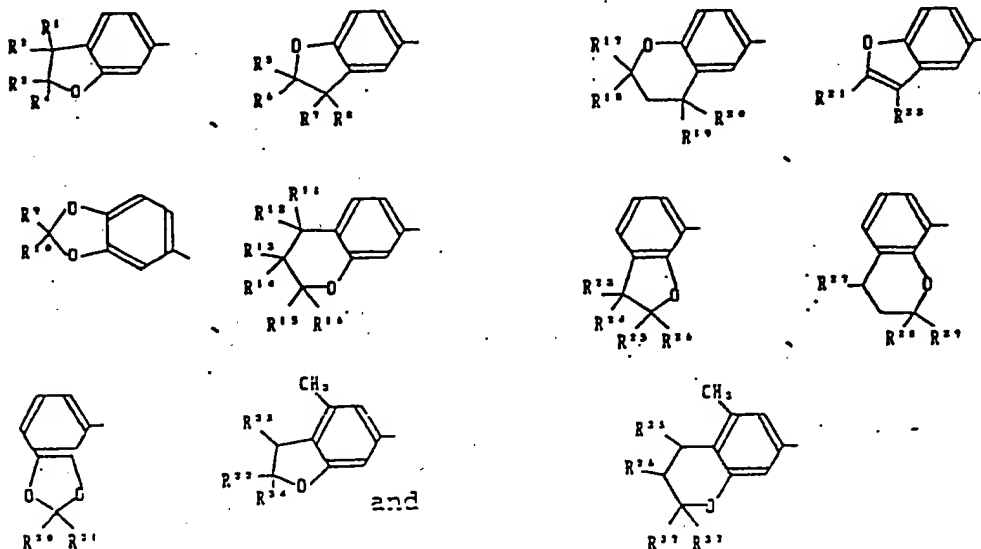
wherein Ar and A are as defined above, and B is a hydrogen atom, a methyl or methoxy radical can be produced from the aromatic amine derivatives of the present invention by the method described in Japanese Patent Application No. 61-177858 (WO 87/00840) which is assigned to the same assignee as the present invention and whose disclosure incorporated herein by reference. The compounds of formula [IV] are effective as herbicides as described in Japanese Patent Application No. 61-177858 (WO 87/00840). The specification of the Application reports the measured physical properties of the compounds, to which the measured physical properties of the aromatic amine derivatives of the present invention conform.

Claims

1. An aromatic amine derivative of the general formula [I]:



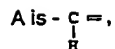
wherein Ar is a radical selected from the group consisting of



wherein R¹ to R¹⁵ and R¹⁷ to R³⁸ may be the same or different and are independently selected from the group consisting of hydrogen, lower alkyl radicals, and lower alkoxy radicals, R¹⁶ is selected from the group consisting of hydrogen, lower alkyl radicals, lower alkoxy radicals and hydroxyl, with the proviso that R² and R³, R⁶ and R⁷, R⁹ and R¹⁰, R¹¹ and R¹⁶, or R¹⁵ and R¹⁶ may, taken together, represent an alkylene chain, which may be substituted with a lower alkyl radical, to form a 5- or 6-membered ring with the carbon atoms to which they are attached, R¹¹ and R¹² may, taken together, represent an ethylene dioxyl radical, or R¹⁴ and R¹⁵ may, taken together, represent a dichloromethylene radical; and

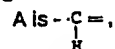
A is a nitrogen atom or $-\text{C}-\text{X}$

wherein X is selected from the group consisting of a hydrogen atom, a chlorine atom, a nitro radical, and a trifluoromethyl radical, when both R⁵ and R⁸ are methyl radicals and



at least one of R^7 and R^8 does not represent hydrogen atom, when both R^{25} and R^{26} are methyl radicals
and

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at least one of R^{23} and R^{24} does not represent hydrogen atom.

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EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 88301000.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB - A - 1 192 002 (JCJ) * Formula I *	1	C 07 D 307/83 C 07 D 311/58 C 07 D 317/46
A	EP - A1 - 0 118 794 (ALKALOIDA VEGYÉSZETIGYÁR) * Claim I; examples 5, 11, 86 *	1	C 07 D 405/12
A	DE - C3 - 2 734 148 (KONISHIROKU) * Formula I, II, III; example 13 *	1	
A	US - A - 4 120 871 (GATES) * Claim 1; abstract *	1	
A	EP - A1 - 0 059 884 (SCHERING) * Formula I *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 98, no. 1, January 3, 1983, Columbus, Ohio, USA ITO, KAZUO; IIDA, TOSHIYUKI; ICHINO, KAZUHIKO; TSUNEZUKA, MASA; HATTORI, MASSAO; NAMBA, TSUNEO; "Obovatol and obovatol, novel bi- phenyl ether lignans from the leaves of Magnolia obovata Thunb." page 250, column 1, abstract no. 2 740p & Chem.Pharm.Bull. 1982, 30(9), 3347-53	1	C 07 D 307/00 C 07 D 311/00 C 07 D 317/00 C 07 D 405/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 25-04-1988	Examiner HAMMER
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			



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EUROPEAN SEARCH REPORT

Application number

-2-

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 88301000.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	CHEMICAL ABSTRACTS, vol. 81, no. 8, August 26, 1974, Columbus, Ohio, USA USTINO, V.A.; MIRONOV, G.S.; FARBEROV, M.I.; KRYUKOVA, G.G.; "Synthesis of aminopolycarboxylic acids and anhydrides." page 1, column 2, abstract no. 37 845c & Uch.Zap. Yaroslav. Tekhnol.Inst. 1972, 22(2), 44-55 -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 25-04-1988	Examiner HAMMER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

Table 3 (contn'd)

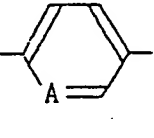
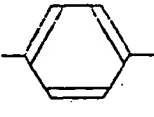
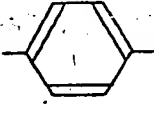
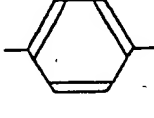
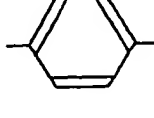
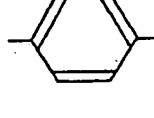
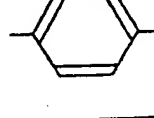
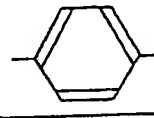
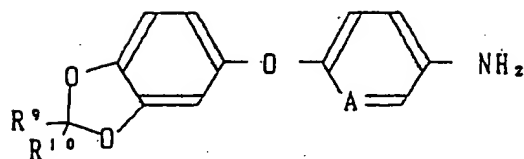
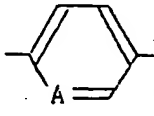
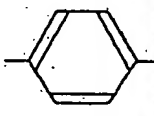
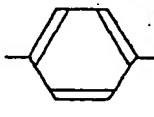
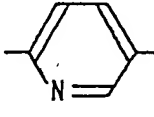
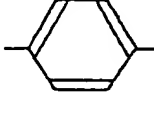
Compound No.	R ⁹	R ¹⁰	
5 5	OC ₂ H ₅	CH ₃	
5 6	OC ₂ H ₅	C ₂ H ₅	
5 7	OCH ₃	H	
5 8	OC ₂ H ₅	H	
5 9	CH ₃	C ₃ H ₇ ⁱ	
6 0	C ₂ H ₅	C ₂ H ₅	
6 1	-(CH ₂) ₄ -		

Table 3



Compound No.	R^9	R^{10}	
5 0	H	H	
5 1	C_2H_5	CH_3	
5 2	CH_3	CH_3	
5 3	CH_3	CH_3	
5 4	OCH_3	CH_3	